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Decomposition Studies of Triphenylboron, Diphenylborinic Acid and Phenylboric Acid in Aqueous Alkaline Solutions Containing Copper

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DECOMPOSITION STUDIES OF TRIPHENYLBORON, DIPHENYLBORINIC ACID AND PHENYLBORIC ACID IN AQUEOUS ALKALINE SOLUTIONS CONTAINING COPPER (U)

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SUMMARY

This report documents the copper-catalyzed chemical kinetics of triphenylboron, diphenylborinic acid and phenylboric acid (3PB, 2PB and PBA) in aqueous alkaline solution contained in carbon-steel vessels between 40 and 70 °C. The following summarizes the results.

- Kinetic expressions developed from this study for 3PB solutions with only added copper yield lower decomposition rates than rates observed in recent (i.e., October of 1995 to present) Tank 48H measurements.
- Kinetic expressions developed from this study for both 2PB and PBA solutions with only added copper indicate decomposition rates of the same order of magnitude as those observed from the Tank 48H measurements.
- The relative rate of decomposition increases in the order of 3PB < PBA < 2PB.
- Tests at 40 °C containing the highest Cu (10 mg/L added $CuSO_4 \cdot 5H_2O$) showed the following ranges of decomposition over 400 to 500 hours of testing: 3PB (25 to 75%), 2PB (100%) and PBA (50 to 100%).
- All three intermediates are relatively stable (≤ 5% decomposition) over ~500 hours when contained in air-sealed carbon-steel vessels at ambient temperature (23-25 °C) with no added copper present.
- The rate of decomposition increased significantly with increasing temperature, decreasing the time for complete decomposition of the intermediates from over 500 hours at 40 °C to between 50 and 300 hours at 70 °C with otherwise identical conditions.
- The dependence of decomposition for the various intermediates on amount of added copper increases in the order of 3PB < 2PB < PBA.
- Limited experiments to explore the role of oxygen in PBA decomposition suggest an important role for oxygen in this reaction sequence. However, additional testing is required to fully elucidate this dependence.

These findings prompt the following recommendations.

- Researchers should pursue additional studies to examine the decomposition rate of triphenylboron under a broader set of catalytic environments including the presence of other suspected catalysts with varying oxygen content.
- Parallel tests, in progress, examine the role of oxygen in the copper-catalyzed decomposition of phenylboric acid. Depending on the results from those tests, additional tests may prove useful in elucidating the kinetics.

INTRODUCTION

The In-Tank Precipitation (ITP) process started operation in Tank 48H by addition of 37,300 gallons of NaTPB solution to Tank 48H in September of 1995.[1] The ITP process encountered high rates of sodium tetraphenylborate decomposition and resulting benzene generation approximately 2-3 months after additions of the tetraphenylborate reagent.[1-2] Sodium tetraphenylborate exhibits known instability resulting in decomposition in the presence of copper.[3] Recent work indicates excess sodium tetraphenylborate in Tank 48H is susceptible to decomposition, with the rate strongly influenced by temperature.[4] Postulated mechanisms for the decomposition of soluble TPB^- include a progression from the tetraphenylborate (TPB^-) through triphenylboron (3PB or $(C_6H_5)_3B$), diphenylborinic acid (2PB or $(C_6H_5)_2BOH$) and phenylboric acid (PBA or $C_6H_5B(OH)_2$), ultimately leading to the stable products of phenol, benzene and boric acid.[1] Modeling the overall decomposition requires a fundamental understanding of each individual reaction step for the intermediates produced from TPB^- decomposition. Therefore, it is necessary to determine the reactivity of each 3PB, 2PB and PBA component in copper-containing alkaline solution.[5] Similar testing involving aqueous alkaline copper solutions of the parent TPB^- was performed in a separate study by M. J. Barnes.[6]

This report describes kinetic investigations to determine reaction rates and decomposition products of 3PB, 2PB and PBA in aqueous alkaline solution in the presence of soluble copper ion between 40 and 70 °C. Appendix A provides a summary of known literature accounts, prepared in part by Dr. R. Bruce King of the University of Georgia, describing the chemistry of these three intermediates with OH^-, H_2O (i.e., hydrolysis) and potential metal catalysts. This study uses a statistically designed matrix (see Appendix B).[7] These kinetic tests investigated the influence of four test parameters (i.e., temperature, organic reagent, hydroxide and copper) towards overall reactivity using a test set of ten experiments for each organic reagent. Rate expressions derived from the initial decay slopes of the concentration versus time plots for each organic component provide relative decomposition comparisons for the three organic components under identical reaction conditions. Results of this study are discussed below. Appendix C details the experimental methods.

Decomposition Reactions for Oxidation and Hydrolysis

The three organic species in aqueous alkaline solution likely exist in equilibrium with their corresponding tetracoordinate anionic species (see discussion of Preliminary Literature Search by Dr. R. Bruce King in Appendix A). For demonstration purposes, this section shall focus on the relevant reactions for the decomposition of 3PB. However, one may postulate identical reaction pathways for all three intermediate species. One may represent the equilibrium reaction for 3PB by:

$$3PB + OH^- \iff [(C_6H_5)_3B(OH)]^- \qquad (1)$$

In the presence of copper, overall stoichiometric reactions of the three coordinate neutral species (3PB) to produce phenol (requiring oxidation) and benzene (requiring hydrolysis) become:

$$2(3PB) + O_2 + 2H_2O \xrightarrow{Cu^{n+}} 2(C_6H_5)_2BOH + 2C_6H_5OH \quad (2)$$

$$3PB + H_2O \xrightarrow{Cu^{n+}} (C_6H_5)_2BOH + C_6H_6 \quad (3)$$

In Equations 2 and 3, Cu^{n+} represents soluble copper of unknown oxidation state. Identical reaction pathways can be postulated for the four coordinate anions (i.e., the parallel of reactions for the product species in Equation 1), and should also be considered when evaluating likely reaction sequences. This discussion omits these parallel pathways of the reaction for brevity.

Barnes recently discussed various decomposition reactions involving different forms and oxidation states of soluble copper with tetraphenylborate anion in alkaline solution (see reactions #2-7 of Ref. #6). An extension of these considerations also applies for copper-catalyzed reactions of the various intermediates discussed above. Generally the reactions involve oxidation of the organic by the tetrahydroxy copper(II) anion. Using 3PB as an example, one writes this reaction as follows.

$$3PB + 2Cu(OH)_4^{2-} \rightarrow 2Cu(OH)_2^{-} + (C_6H_5)_2BOH + C_6H_5O^{-} + OH^{-} + H_2O \quad (4)$$

The dihydroxy copper(I) anion formed in reaction 4 can oxidize in the presence of oxygen.

$$4Cu(OH)_2^{-} + 4OH^{-} + 2H_2O + O_2 \rightarrow 4Cu(OH)_4^{2-} \quad (5)$$

In a second pathway, again using 3PB as an example, the reduced form of Cu functions as a catalyst to promote 'dephenylation' of the organic intermediates.

$$3PB + Cu(OH)_2^{-} \rightarrow (C_6H_5)_2BOH + Cu(C_6H_5)(OH)^{-} \quad (6)$$

$$Cu(C_6H_5)(OH)^{-} + H_2O \rightarrow Cu(OH)_2^{-} + C_6H_6 \quad (7)$$

Note that this discussion does not address free radical chemistry. Other reaction pathways can be postulated based on free radical chemistry. However, identification of such pathways is beyond the scope of this report and will be addressed in future work.

RESULTS AND DISCUSSION

Ten experiments were performed within a statistically designed matrix (see Appendix B) for each of the organic components. Two additional control samples containing nominal amounts of organic, 1.5 M OH^- and no added copper were held at ambient temperature (23-25 °C) for the duration of each set of experiments. These two control samples, not part of the statistically designed matrix, serve to indicate the ambient temperature stability of the various organic components in air-sealed alkaline aqueous solution. Appendices D through F contain analytical data for tests involving 3PB, 2PB, and PBA, respectively. All data shown in Appendices D-F are for air-sealed systems. The same vessel numbering sequence was used for each of the different organic component test series (see Table B-1 of Appendix B).

One set of additional tests was also performed for the PBA component. These additional PBA tests, identified as PBA Series #2, investigated the effects of nitrogen-purges on the decomposition of PBA. Appendix G provides data for the

Series #2 PBA tests. Discussion of the results will first address the rate expressions developed for each intermediate. The relative reactivities of 3PB, 2PB and PBA are then compared. Finally, the kinetic expressions developed in the present tests are compared to recent kinetic fitting of Tank 48H data.

Rate Expressions

Inspection of the experimental data (see Appendices D through F) indicates that significant decomposition of these species occurs under the present test conditions. As further explained in Appendix B, these tests investigate the role of temperature, copper concentration and hydroxide ion concentration on the rate of decomposition of these species. Typically, a kinetic rate equation expresses the dependence of the reaction on these parameters. These expressions usually assume the form:[8]

$$\frac{d[x_s]}{dt} = -k[x_s]^a[Cu^{n+}]^b[OH^-]^c \tag{8}$$

with:

$$k = A * e^{\frac{E_A}{RT}} \tag{9}$$

where: $[x_s]$ = the concentration of the species of interest

$[Cu^{n+}]$ = the concentration of copper (Note: Cu^{n+} = soluble copper of unknown oxidation state)

$[OH^-]$ = the hydroxide ion concentration

a,b,c = order of reaction for each respective component
k = rate constant
A = pre-exponential factor
E_a = activation energy
R = gas constant (8.314 $JK^{-1}mole^{-1}$)
T = temperature (K)

Using the data in Appendices D through F, the authors estimated the reaction rate constants. The authors assume these degradation reactions to vary linearly with the concentration of the organic species. Therefore, holding the copper concentration, hydroxide concentration and temperature constant throughout an experiment, one integrates Equation 8 to produce:

$$\frac{[x_s]}{[x_s]_o} = e^{-k[Cu^{n+}]^b[OH^-]^c t} \tag{10}$$

One may evaluate this expression with respect to the experimental data to obtain estimates of the rate expression parameters. This evaluation was performed for each of the reactive systems to produce rate expressions. Appendix H contains the experimental data employed in this evaluation and the estimated values and error functions for these fits. The following text discusses each of these expressions in turn. In performing these analyses, the order of reaction for all of the individual organic components was assumed equal to one. This assumption proves consistent with most of the rate expressions that could be derived from the proposed reaction sequences.

3PB Decomposition

Analyses of the experimental data for the decomposition of 3PB indicated that hydroxide does not play a statistically significant role in the degradation reaction. However, the decomposition reaction showed an approximate 1/3 order dependence on total copper concentration. Equation 11 represents the rate expression for the best fit of the experimental data.

$$\frac{d[3PB]}{dt} = -1.7x10^{12} * e^{\frac{-82,200}{RT}} \left[Cu^{n+}\right]^{0.4} [3PB] \qquad (11)$$

Note: This and all subsequent rate expression use concentrations in molar units.

Equation 11 also indicates an activation energy for this reaction of 82,200 J/mole. Note that a significant level of uncertainty (at least 20%) exists in both the activation energy and the reaction copper order. However, this analysis suggests a reaction copper order significantly different from unity. An integer copper order implies that only a single reaction provides the rate limiting step in the reaction pathway. The observed deviation from unity suggests a combination of the proposed reactions provides a more likely pathway for this decomposition. However, this analysis uses a basis of the total concentration of copper added to the system, not the measured soluble copper concentration. Therefore, the conclusion regarding the dependence on copper concentration order may change when considering only soluble copper as a catalyst.

Inspection of Equations 4 through 7 indicate hydroxide appears as a reactant only in Equation 5. The lack of hydroxide dependence for the 3PB decomposition rate suggests the reaction in Equation 5 either does not play a significant role in the decomposition of 3PB or happens quickly and thus does not govern the overall reaction rate.

Results in Appendix D show that 2PB and PBA concentrations are below or only slightly above the detection limits in the reaction mixture during decomposition of 3PB. This result suggests that the decomposition of these intermediates procedes significantly faster than the copper catalyzed decomposition of the 3PB.

Further inspection of Appendix D shows, for all reactions when significant decomposition of 3PB was observed, measurable quantities of both phenol and benzene formed. Only with large quantities of 3PB introduced under highly reactive conditions (i.e., 70 °C) did the reaction system produce more benzene produced than phenol. This result suggests, under these conditions, possible depletion of the oxygen concentration in the solution by the rapid formation of phenol, thereby shifting the reaction products to benzene. Cast in terms of Equations 4 through 7, this result suggests that all of the reaction pathways may play a significant role in the degradation of 3PB. However, one requires additional tests to illuminate the impact of each individual pathway. Furthermore, any conclusions drawn from the product split becomes obscured by the role of the other intermediates formed upon the decomposition of 3PB.

2PB Decomposition

Similar to 3PB, the decomposition of 2PB does not depend significantly on the hydroxide concentration. Analysis of the data shows the 2PB decomposition depends on copper to the approximately 1/2 order. Equation 12 represents the rate expression for the best fit of the experimental data.

$$\frac{d[2PBA]}{dt} = -9.4x10^{13} * e^{\frac{-82,100}{RT}} \left[Cu^{n+}\right]^{0.5} [2PB] \qquad (12)$$

As indicated in Equation 12, the analysis provides an activation energy for this reaction of approximately 82,100 J/mole. Similar uncertainty (20 %) exists in the activation energy and copper order for this reaction. This leads to similar conclusions drawn from the observed copper order and lack of hydroxide dependence as noted for the 3PB decomposition reaction. These results suggest a combination of the proposed reaction steps involved in governing this decomposition reaction.

Some additional insight can be drawn from the analysis of the reaction products. Inspection of Appendix E shows that 2PB decomposition tends to produce proportionally more benzene than phenol compared to the 3PB decomposition data shown in Appendix D. Phenol was found as the primary product only when using higher hydroxide concentrations and low initial 2PB concentrations. This result suggests the reaction pathway of Equations 4 and 5 predominates at high hydroxide concentrations in the presence of soluble oxygen, but that the pathway expressed by Equations 6 and 7 may predominate outside these conditions.

Note the measurable quantities of PBA found during many of these 2PB copper catalyzed decomposition experiments. This result suggests that, with copper as the only catalyst present, the PBA decomposes at a rate of a similar order of magnitude as 2PB, in contrast to the significantly slower rate for 3PB.

PBA Decomposition

The decomposition of PBA differs significantly from the decomposition of 2PB and 3PB. Equation 13 represents the rate equation for the best fit of the experimental data.

$$\frac{d[PBA]}{dt} = -9.4x10^{18} * e^{\frac{-107,000}{RT}} \left[Cu^{n+}\right]^{0.9} \left[OH^{-}\right]^{0.7} [PBA] \qquad (13)$$

Comparison of Equation 13 with Equations 11 and 12 shows the differences. In particular, note the presence of a hydroxide dependence in Equation 13 and the near unity copper order for this rate expression. Considered in context of the proposed reaction pathways, this analysis suggests PBA most likely decomposes by the pathway represented by Equations 4 and 5. In addition, inspection of the data in Appendix F shows phenol as the primary product in all but one of the systems experiencing extensive reaction.

Researchers repeated the first four vessel tests at 40 °C of the initial air-sealed PBA series (see V#1-4 in Appendix F) in the second PBA series with nitrogen inerting of the ~60 mL vapor space above the solutions immediately before sealing the samples (see Series #2, V#1-4-N2 in Appendix G). These vapor-space inerted tests did not rigorously exclude oxygen since the researchers made no effort to dessicate the solutions and introduced ~ 5 cc of air into the samples with each analysis step. In the presence of low 0.1 mg/L total added copper, very little decomposition occurred for either the air-sealed (V#1,#4) or the nitrogen-inerted (V#1-N2, V#4-N2) tests. In the presence of high 10 mg/L total added copper, inerting the vapor space had the apparent effect of both slowing the overall rate of PBA decomposition and changing the final product distribution from predominately phenol (air-sealed) to benzene (nitrogen-inerted). One interpretation of these results suggests that inerting shifts the dominant reaction pathway from Equations 4-5 to Equations 6-7. If Since PBA decomposition accelerates in the presence of oxygen (both as dissolved oxygen and as oxygen present in air sealed above the reaction mixture), future tests should consider additional measures of oxygen removal involving solution inerting and replacement of air (contained in the sampling syringe) with nitrogen during sample analysis. Note that parallel testing currently underway to explore this role of oxygen in PBA decomposition appears to support this conclusion.[9]

Comparison of Intermediate Rate Expressions

The decomposition rates of the various intemediates increase in the order of 3PB < PBA < 2PB. The order of dependence on total copper increases in the order of 3PB < 2PB < PBA. The copper order for the sucessive reactions overlap at the 95 % confidence interval, however a significant difference exists between the copper orders for 3PB and PBA. These analyses also indicate the activation energies for these systems fall between 82 and 107 kJ/mole and increase in the order of 3PB ≈ 2PB < PBA. Given the similarities in the activation energies and copper dependence for 2PB and 3PB, one might conclude that these reactions occur through similar pathways. However, one requires further testing to verify this assumption with any signifcant level of certainty.

Researchers found no statistically significant dependencies on the hydroxide concentration over the range of 0.5 - 2.5 M OH^- in these tests for 2PB and 3PB. However, a fractional positive order dependence for PBA was found. This dependence may reflect either an increase in solubility of copper as a function of hydroxide concentration (see for example Ref. #1 and #6) or it may reflect hydroxide ion playing a role in the reaction kinetics. Final test solution analyses for soluble copper continue for the present study (see Appendix C). These measured soluble copper values may further clarify the proposed influence of copper solubility on the fractional positive order dependence for PBA decomposition. However, at this time, on may not differentiate between homogeneous and heterogeneous catalysis of these reactions by copper. Furthermore, some inconsistencies exist within the data set with respect to the dependence on hydroxide. Therefore, while the reported rate expression contains a hydroxide term, the role of hydroxide in this reactive system remains uncertain.

Comparison of Present Study Kinetics to Tank 48H Data

One may use expressions shown above to calculate rate constants for decomposition of the organic components under specific solution conditions. Table 1 shows the calculated rate constants for decomposition of each organic species at 25 °C. These rate constants represent the value k in Equation 8. Note the partial order of this rate constant due to the non-integer dependence on copper concentration, as shown in Table 1 with units of $M^{-b}hr^{-1}$.

TABLE 1. Comparison of Copper-Catalyzed Rate Constants for Organics Decomposition to PVT-1 and TK-48H Kinetic Fits

Organic Component	Calculated Rate Constant (k) $M^{-b}hr^{-1}$ (25°C)	Calculated Apparent-First Order Rate Constant (k') hr^{-1} (25°C)	PVT-1 Tank* 48H Measured First Order Rate Constant hr^{-1} (25°C)	Batch #1 Tank 48H Measured Rate Constant hr^{-1} (25°C)
3PB	3.92E-03	1.57E-04	1.72E-03	4.50E-04
2PB	2.49E-01	3.41E-03	1.15E-04	2.80E-03
PBA	1.648	2.00E-4	1.14E-04	2.50E-04

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* These rate constants represent interim results of a continuing global effort to determine the rate expressions for the reactions. The authors anticipate further work will provide additional resolution to these values and, as such, did not pursue a complete technical review of these values.

Casting these rate constants as apparent first-order rate constants based on fixed copper concentration aids the comparison.

$$k' = k*[Cu^{n+}]^b \qquad (14)$$

Table 1 presents these apparent rate constants. The calculated rate constants assume a copper concentration of 1.4 mg/L (or 2.2 E-5M) and hydroxide concentration of 2.5 M. These concentrations represent those measured in Tank 48H during the Fall of 1995.[10] More recent analyses of the soluble copper and hydroxide concentration in Tank 48H show lower concentrations (copper ≈ 0.3 mg/L and hydroxide ≈ 1.3 M). Table 1 includes two attempts to estimate first order rate constants based on available Tank 48H data. The initial estimate uses PBA measurements taken from Tank 48H from November of 1995 through May of 1996.[1] The last column shows estimates of first-order rate constants from this analysis. More recently, researchers developed analytical high pressure liquid chromatography (HPLC) methods to quantitatively measure all three species (3PB, 2PB and PBA) in Tank 48H.[11] Process Verification Testing Phase 1 (PVT-1) included several measurements of these concentrations.[12] Analysis of these data produce estimates of the apparent first-order rate constants for each species as presented in the third column of numerical values of Table 1.

Reasonable agreement exists between the calculated apparent first-order rate constants for 2PB and PBA from this study and the Batch #1 estimates. Reasonable agreement also exists for PBA between the rate constant calculated from this study and that observed during PVT-1. However, a significant difference exists for 2PB between the rate constants from this work and observed during PVT-1. This difference may result from the decrease in the copper concentration in Tank 48H. In contrast, one estimates the rate constant for the degradation of 3PB in Tank 48H higher than from the present study. This result suggests that perhaps some species other than copper may result in the degradation of 3PB. Alternatively, the effect of oxygen as an inhibitor towards copper-catalyzed 3PB decomposition may result in this discrepancy.

CONCLUSIONS

Researchers studied the copper-catalyzed chemical kinetics of triphenylboron, diphenylborinic acid and phenylboric acid (3PB, 2PB and PBA) in aqueous alkaline solution contained in carbon-steel vessels between 40 and 70 °C. The results show the stability of all three intermediates in alkaline solution (pH ≥ 13) when kept at ambient temperature in the absence of copper. At 40 °C and total added copper of 10 mg/L, approximately 25 to 75% of 3PB decomposed, ~100% of 2PB decomposed and approximately 50 to 100% of PBA decomposed within 500 hours. All three species completely decomposed at 70 °C with total added copper of 10 mg/L within 300 hours.

Kinetic expressions developed from the present study with added copper indicate lower decomposition rates than observed in recent (i.e., October of 1995 to present) Tank 48H measurements for 3PB. Similar kinetic comparisons indicate 2PB and PBA decomposition rates found in the present study of almost the same order of magnitude as observed from the Tank 48H measurements. The relative rate of decomposition increases in the order of 3PB < PBA < 2PB. The dependence of decomposition on amount of added copper increases in the order of
3PB < 2PB < PBA.

Preliminary examination of the reaction pathways suggest that the copper catalyzed degradation of 3PB and 2PB occur through similarly rate limiting steps. However, these analysis suggest that the oxidation of copper may play a more significant role in governing the rate of decomposition of PBA in the presence of oxygen.

Nitrogen-purging of the vapor-space above PBA samples reduces overall rates of PBA decomposition and changes the product yield from predominately phenol (air-sealed) to benzene (nitrogen-purged).

Either phenol or benzene occurs as the predominant final organic product obtained in present decomposition studies of 3PB and 2PB, depending on specific reaction conditions. Phenol exists as the predominant final organic product obtained in the copper-catalyzed decomposition of PBA.

Further Work

Additional work will investigate the effect of other potential catalysts on the decomposition of 3PB, 2PB and PBA. These studies will repeat some of the present tests with additional additives such as solid sludge components containing noble metals, monosodium titanate solids, and other soluble metal ions. Researchers will select these additives from a group of possible catalysts previously identified in tetraphenylborate decomposition studies.[13,14] These future tests should indicate if other catalytic species, in addition to copper, significantly contribute to destruction of 3PB, 2PB and PBA. Also, repetition of selected tests in this study for 3PB, 2PB and PBA using more stringent means of oxygen removal and prevention of air exposure during sampling, would study copper-catalyzed decomposition of the intermediates under inerted conditions more applicable to waste tank conditions of
~ 5 vol % air.

QUALITY ASSURANCE

The experimental methods and results were recorded in laboratory notebook WSRC-NB-95-308. The task plan and quality assurance plans are:

C. L. Crawford, "Task Technical Plan for Decomposition Studies of Triphenylboron, Diphenylborinic Acid and Phenylboric Acid in Aqueous Alkaline Solutions Containing Copper (U)", **WSRC-RP-96-568, Rev.** 0, November 5, 1996.

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APPROVALS

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Appendix A

Relevant Literature Review of 3PB, 2PB and PBA Chemistry

Reactions of the various organic intermediates with hydroxide ion, water (i.e., hydrolysis) and potentially catalytic metals found in nuclear wastes are discussed below. First, some relevant literature accounts of 3PB are cited. Next, preliminary literature searchs prepared by Dr. R. Bruce King of the University of Georgia (Athens, GA) concerning both 3PB chemistry and also 2PB and PBA chemistry are then presented.

Triphenylboron is reported to hydrolyze rapidly in dilute alkaline solution.[1] However, a 9 wt % aqueous solution of a sodium hydroxide adduct of 3PB (reagent grade chemical) is manufactured by DuPont and is also available in laboratory quantities from Aldrich Chemical Company.[2] Aqueous 3PB is apparently stabilized and is not subject to decomposition in highly caustic aqueous media. The reactivity information contained in the Material Safety Data Sheets for the 3PB·NaOH adduct lists only an incompatibility with 'strong oxidizing agents'.[3]

Different accounts of the stability of 3PB towards hydrolysis are given by Sidgwick[4] and Simon[5] compared to the results of Brown and Dodson.[1] Sidgwick and Simon report that 3PB is inert towards hydrolysis while Brown and Dodson have shown that 3PB decomposes over an 8 hr period when kept in contact with distilled water. These reported differences in neutral aqueous 3PB stability could depend on the presence of oxygen. Simon asserts that dissolved oxygen present in neutral aqueous 3PB solutions promotes hydrolysis reactions that decompose 3PB. Such hydrolysis of 3PB was not observed by Simon when oxygen was rigorously excluded from solution.

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[4] N. V. Sidgwick, The Chemical Elements and their Compounds, Vol. I., Oxford University Press, London, **1949**, 370.

[5] V. A. Simon, "The Protolysis of the Tetraphenylboron Anion", Ph. D. Dissertation, Florida State University, FL, **1962**.

Triphenylboron Chemistry in Basic Aqueous Media

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The chemistry of triphenylboron, $(C_6H_5)_3B$, in alkaline aqueous solution is of interest in connection with understanding the decomposition of tetraphenylborate in basic high level nuclear waste media. In alkaline aqueous media triphenylboron exists as its hydroxide adduct hydroxytriphenylborate, $(C_6H_5)_3BOH^-$, arising from the following equilibrium:

$$(C_6H_5)_3B + OH^- \rightleftarrows (C_6H_5)_3BOH^- \qquad (1)$$

Both triphenylboron (called "triphenylborane" in the Chemical Abstracts nomenclature since "BH_3" is called "borane") and hydroxytriphenylborate were searched in the Chemical Abstracts substance index during the period 1967–1995, inclusive, in order to assemble any relevant literature information. Patents are not readily available in the University of Georgia library and thus were not consulted in original form.

Relatively little relevant information was found in this search. However, the following items are of possible interest:

(1) The salt $Li[(C_6H_5)_3BOH]\cdot(C_2H_5)_2O$ is obtained from triphenylboron and lithium hydroxide in the presence of diethyl ether. Thermal decomposition of this salt is reported[1] to give a dark carbonaceous residue with no fixed composition if the sample is heated at a rate of one degree per minute until constant weight is reached. However, maintaining the sample isothermally at 100°C gives a residue of composition of $Li[(C_6H_5)_2BO]$ apparently by elimination of benzene according to the following equation:

$$Li[(C_6H_5)_3BOH]\cdot(C_2H_5)_2O \xrightarrow{\Delta} Li[(C_6H_5)_2BO] + C_6H_6 + (C_2H_5)_2O \qquad (2)$$

(2) Hydroxytriphenylborate has been patented[2] as a precipitant for removal of cesium suggesting that $CsB(C_6H_5)_3OH$ is insoluble like $CsB(C_6H_5)_4$.

(3) An alkaline solution containing a mixture of hydroxytriphenylborate and the dihydroxydiphenylborate ion derived from diphenylborinic acid upon acidification

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[1] Fields, C. L.; Patnoe, R. L.; Leschnik, D., Thermal Decomposition of Organoborate Salts, *Anal. Calorim.*, 1977, *4*, 91-93.

[2] Sullivan, J. M., U. S. 5,144,063 (1992).

precipitates triphenylboron at pH 7.6 when diphenylborinic acid still remains in solution. This has been patented[3] as a method for separating triphenylboron from diphenylborinic acid and implies that $H[(C_6H_5)_3BOH]$ is a weaker acid than $H[(C_6H_5)_2B(OH)_2]$.

(4) Triphenylboron and sodium methoxide are patented[4] to give sodium tetraphenylborate above 200°C presumably by the following reaction:

$$4\,(C_6H_5)_3B + 4\,NaOCH_3 \longrightarrow 3\,NaB(C_6H_5)_4 + NaB(OCH_3)_4 \qquad (3)$$

This is probably the patent that was uncovered by George Parshall several months ago.

(5) The anodic oxidations of a variety of trialkyl- and triarylborons has been investigated electrochemically in acetonitrile solution using sodium tetrafluoroborate as the supporting electrolyte.[5,6] Triarylborons were found to be more readily oxidized under such conditions than trialkylborons even though the lower trialkylborons such as $(CH_3)_3B$ and $(C_2H_5)_3B$ are spontaneously flammable in air in contrast to triarylborons. The anodic oxidations of the triarylborons were irreversible and were suggested to involve the generation of radical cations followed by removal of aryl groups by sequences of the following type (e.g., $R = C_6H_5$):

$$R_3B \xrightarrow{-e} R_3B^{\bullet +} \longrightarrow R_2B^{+} + R^{\bullet} \qquad (4)$$

The irreversible oxidation potential for triphenylboron of 2.04 V is reduced to ~1.5 V upon complexation with ammonia or pyridine.

(6) Two environmentally oriented papers from the Savannah River Ecology Laboratory (SREL) on the decomposition of sodium tetraphenylborate discuss triphenylboron intermediates. Hunter and Bertsch[7] measure the surface-facilitated degradation of tetraphenylborate in fully aquated clay pastes using attenuated total reflectance Fourier transform infrared spectroscopy. Surface-facilitated oxidation of tetraphenylborate to diphenylboronic acid was observed at Lewis acid sites on clay mineral surfaces on three members of the smectite family of clays, which contained iron in the structure. In addition, the degradation of tetraphenylborate to triphenylboron at Brønsted acid sites was measured on aluminum-saturated clays. First-order rate models were developed for both reactions. The pH range in these experiments is relatively acid compared with the strongly alkaline

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[3] Seidel, W> C., U. S. 4,177,215 (1979).

[4] Peet, W. G.; Tebbe, F. N., U. S. 4,510,327 (1985).

[5] Urtaeva, Zh. Kh.; Bumber, A. A.; Okhlobystin, O. Yu., *Dokl. Akad. Nauk. SSSR Engl. Transl.*, 1986, *286*, 85-88.

[6] Urtaeva, Zh. Kh.; Bumber, A. A.; Okhlobystin, O. Yu., *Zhur. Obshch. Khim. Engl. Transl.*, 1986, *56*, 1142-1146.

[7] Hunter, D. B.; Bertsch, P. M., *Environ. Sci. Technol.*, 1994, *28*, 686-691.

nuclear waste media currently of interest. However, this study might suggest possible reactions on the solid hydrous oxides present in the sludges.

The other paper from SREL by Mills and Sullivan[8] studies the indirect photolysis of tetraphenylborate initiated by humic substances in natural waters. Triphenylboron, o-terphenyl, and diphenylborinate were identified as degradation products in solvent extracts of irradiated solutions using gas chromatography/mass spectrometry.

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[8] Mills, G. L.; Sullivan, L. R., *Chemosphere*, 1995, *31*, 4541-4547.

Chemistry of Phenylboronic Acid and Diphenylborinic Acid in Basic Media: A Preliminary Literature Search

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September, 1996

The following aspects of the chemistry of phenylboronic acid, $C_6H_5B(OH)_2$, and diphenylborinic acid, $(C_6H_5)_2BOH$, are of interest and relevance in connection with understanding their roles as intermediates in the decomposition of tetraphenylborate in basic high level nuclear waste media:

(1) Reactions of $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ with hydroxide ion in basic media to give the corresponding tetracoordinate anions, i.e.

$$C_6H_5B(OH)_2 + OH^- \rightleftarrows [C_6H_5B(OH)_3]^- \qquad (1a)$$
$$(C_6H_5)_2BOH + OH^- \rightleftarrows [(C_6H_5)_2B(OH)_2]^- \qquad (1b)$$

(2) Information relating to the hydrolysis of $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ to benzene and boric acid in basic media.

(3) Interactions with $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ in basic media with metals found in nuclear wastes.

Phenylboronic acid and diphenylborinic acid were searched in the Chemical Abstracts substance index during the period 1967–1995, inclusive in order to assemble any relevant literature information on these topics. Most of the relatively few papers of possible relevance found during this search traced back to a fundamental 1882 paper by Michaelis and Becker shortly after the discovery of arylboronic acids.[1] Because of the early date of this paper and its not being readily available in the University of Georgia library, I chose not to take the time to dig it out before preparing this preliminary report.

1. Reactions of $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ with hydroxide ion in basic media

The reaction of $C_6H_5B(OH)_2$ with hydroxide ion (equation 1a) has been studied in detail using temperature-jump relaxation methods.[2] In this connection the second-order rate

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[1] Michaelis, A.; Becker, P., *Ber.*, 1882, *15*, 180.

[2] Kajimoto, O.; Saeki, T.; Nagaoka, Y.; Fueno, T., Temperature-Jump Rate Studies of the Association Reactions of Boric and Benzeneboronic Acids with Hydroxide Ion, *J. Phys. Chem.*, 1977, *81*, 1712–1716.

constants for reaction 1a as well as similar reactions with substituted phenylboronic acids, $XC_6H_4B(OH)_2$ in 0.1 M aqueous KCl medium at 25 and 35°C were measured using the temperature-jump relaxation method. The reactions were found to be activation-controlled process with rate constants on the order of $10^{7-8}M^{-1}sec^{-1}$. The reactivity of phenylboronic acid towards hydroxide ion was found to be greater than that of boric acid. The pK_a for phenylboronic acid at 25°C was found to be 8.70 as compared with 9.24 for boric acid at the same temperature indicating that phenylboronic acid is a less weak acid than boric acid. More recently proton and boron-11 nuclear magnetic resonance methods were used to study reaction equilibria of boronic acids, including phenylboronic acid, with hydroxide ion (equation 1a) in connection with understanding reactions of phenylboronic acid in basic media with 1,2-diols such as 1,2-ethanediol, 1,2-propanediol, and 1,2-dihydroxybenzene.[3] There also appear to be a variety of papers on reactivity of diphenylborinic acid with catecholamines, adrenaline, and other hydroxyamines with basic media which almost certainly involve $[(C_6H_5)_2B(OH)_2]^-$ formed by equation 1b although the papers focused on details of analytical methods based on such reactions rather than the reaction of diphenylborinic acid with hydroxide; these papers did not appear to be very useful for the problems of interest in nuclear waste treatment and thus are not cited in detail.

The following methods were described[4,5] for the preparation of phenylborate salts of the alkali metals (M = Li, Na) and the alkaline earths (M' = Ca, Sr, Ba) in aqueous media:

$$MOH + C_6H_5B(OH)_2 \longrightarrow M[C_6H_5B(OH)_3] \quad (2a)$$

$$M'(OH)_2 + 2\,C_6H_5B(OH)_2 \longrightarrow M'[C_6H_5B(OH)_3]_2 \quad (2b)$$

$$MOH + (C_6H_5)_2BOH \longrightarrow M[(C_6H_5)_2B(OH)_2] \quad (2c)$$

$$M'(OH)_2 + 2\,(C_6H_5)_2BOH \longrightarrow M'[(C_6H_5)_2B(OH)_2]_2 \quad (2d)$$

These salts were characterized by elemental analyses for the metal, boron, carbon, and hydrogen. The thermal decomposition reactions of these salts at temperatures typically up to 150 to 200°C were found to result in the elimination of benzene and water giving ultimately the alkali metal "metaborates," MBO_2. Detailed thermogravimetric data were presented.[5]

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[3] Pizer, R. D.; Ricatto, P. J.; Tihal, C. A., Thermodynamics of Several Boron Acid Complexation Reactions Studied by Variable-Temperature ^1H and ^{11}B NMR Spectroscopy, *Polyhedron*, 1993, *12*, 2137–2142.

[4] Fields, C. L.; Patnoe, R. L.; Leschnik, D., Thermal Decomposition of Organoborate Salts, *Anal. Calorim.*, 1977, *4*, 91–93.

[5] Fields, C. L.; Doyle, J. R., The Thermal Decomposition of Salts of Boronic Acids, *Thermochim. Acta*, 1974, *8*, 239–248.

2. Hydrolysis of $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ to benzene and boric acid in basic media

The final step in the hydrolysis of tetraphenylborate is the conversion of phenylboronic acid to boric acid and benzene. This reaction, which is called a protodeboronation reaction, has been studied in detail in acid solution by Kuivila and his coworker Nahabedian.[6] General acid catalysis has been postulated for these reactions. However, this work is of limited relevance to the decomposition of phenylboronic acid in the basic nuclear waste media because of the vast differences in pH between the pH 13 to 14 nuclear waste media and the highly acid pH range studied by Kuivila and Nahabedian.[6] Of interest, however, is a subsequent study by Hatt[7] of the effect of pH on the stability of phenylboronic acid in aqueous solution. The extent of hydrolysis of phenylboronic acid in aqueous solution at 50° and 100°C was investigated under nonoxidative conditions. All of the samples heated to 100°C for 90 hr. were completely hydrolyzed except for the most alkaline sample (pH 13). The extent of hydrolysis of the samples heated at 50°C for 90 hr. was least for those samples above pH 11, the extent of degradation increasing progressively with lower pH values. Both sets of results show that phenylboronic acid is stabilized by the presence of alkali, at least up to pH 13 where the acid exists as $C_6H_5B(OH)_3^-$ (see equation 1a). This observation was stated to be in accord with much earlier results of Ainley and Challenger[8] who found that phenylboronic acid (1 g) appeared to be unchanged after boiling for 20 hr. with 5% aqueous sodium hydroxide (50 mL).

3. Interactions with $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ in basic media with metals found in nuclear wastes.

No information was found in the literature search on metal complex or salt formation of phenylboronic acid or diphenylborinic acid with ions or hydrous oxides of metals found in the nuclear wastes other than the alkali or alkaline earth metals. For example no information was found in the literature on phenylboronic acid or diphenylborinic acid of their complexes or salts with metals found in high-level nuclear wastes such as iron, manganese, chromium, nickel, zinc, aluminum, etc. There appear to be precedents in the literature for catalytic and/or stoichiometric roles of compounds of metals such as copper and palladium in promoting reactions of phenylboronic acid with

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[6] Kuivila, H. G.; Hanabedian, K. V., Electrophilic Displacement Reactions. X. General Acid Catalysis in the Protodeboronation of Areneboronic Acids, 1961, *83,* 2159–2163.
[7] Hatt, B. W., A Method for Investigating the Effect of pH on the Stability of Benzeneboronic Acid in Aqueous Solution, *Chem. Ind.,* 1975, 617–618.
[8] Ainley, A. D.; Challenger, F., *J. Chem. Soc.,* 1930, 2171.

various inorganic and organic substrates leading to loss of the phenyl group by breaking the phenylboron bond. However, in almost all cases the substrates and reaction conditions are very different than those involved in nuclear waste treatment so that detailed literature information does not appear to be very useful. Mercury compounds also promote very readily the cleavage of the phenyl-boron bond in phenylboronic acid and related compounds to give phenylmercury derivatives.

Summary

(1) Reactions of $C_6H_5B(OH)_2$ and $(C_6H_5)_2BOH$ with hydroxide ion to give the tetracoordinate boron anions $[C_6H_5B(OH)_3]^-$ and $[(C_6H_5)_2B(OH)_2]^-$ have been well described in the literature including rate and equilibrium information. A number of solid alkali and alkaline earth metal salts of these anions have been characterized by standard analytical methods. However, no definitive structural reports on solid metal salts of these anions by methods such as X-ray diffraction were found in the literature search.

(2) Phenylboronic acid appears to be more resistant to hydrolysis in basic rather than acidic media possibly owing to stabilization by formation of the tetracoordinate $C_6H_5B(OH)_3$ anion.

(3) No definite salts or complexes of phenylboronic acid or diphenylborinic acid with metals other than the alkali or alkaline earth metals appear to be reported in the literature. Thus no information appears to be known about salts or complexes of phenylboronic acid or diphenylborinic acid with metals of interest such as iron, manganese, chromium, nickel, zinc, or aluminum.

Appendix B

Statistical Design of Experiments

A typical test matrix for a four parameter system, each of which varies over three levels, is shown in Table B-1. Test series for each organic component involves 10 vessels from the middle portion of the overall test matrix. (see Rows 11 through 20 of Block #2 in Table B-1). Table B-1 uses "-" equal to the lowest level, "0" equal to the middle level, and "+" equal to the highest level of each respective parameter.

The design provided in Table B-1 was generated by the statistical program JMP.[1] It is a blocked, face-centered central composite design.[2] The ten trials comprising Block #2 provide an opportunity to investigate the main effects of the four parameters in the study. The two center points (the '0000' points) provide a check for curvilinear response over the range of factor space studied.[1]

Further sample testing within the overall defined test matrix of Table B-1 involving Blocks #1 (Rows 1-10) and #3 (Rows 21-30) were not specifically planned as a part of this study. Tests involving Block #1 would provide information on the various parameter interactions.[1] Tests involving Block #3 indicate which factors are involved in a curvilinear response.[1] Block #2 sample testing using conditions of gas-space inerting to remove air was conducted on PBA samples.

Chemical analyses results for the 3PB, 2PB and PBA alkaline aqueous systems have been analyzed by visual inspection (see text) to determine the rates of reaction and significant product yields in the presence of copper (added as soluble Cu(II)) and elevated temperatures. The computer program/code "JMP" is currently being used in the detailed analysis of each data set.[1] Any significant differences found in this analysis of the data sets will be documented in a later report.

[1] SAS Institute, <u>JMP Statistics and Graphics Guide</u>, Version 3, SAS Institute Inc., Cary, NC, 1994.

[2] R. L. Mason, R. F. Gunst and J. L. Hess, <u>Statistical Design and Analysis of Experiments with Application to Engineering and Science</u>, John Wiley & Sons, New York, 1989.

Table B-1. Statistically Designed Matrix[a]

Rows	Pattern	Block	Temp.	Organic	OH-	Cu(II)	Test[b] Vessel#
1	---+	1	-1	-1	-1	1	
2	--+-	1	-1	-1	1	-1	
3	-+--	1	-1	1	-1	-1	
4	-+++	1	-1	1	1	1	
5	+---	1	1	-1	-1	-1	
6	+-++	1	1	-1	1	-1	
7	++-+	1	1	1	-1	1	
8	+++-	1	1	1	1	-1	
9	0000	1	0	0	0	0	
10	0000	1	0	0	0	0	
11	----	2	-1	-1	-1	-1	V#1
12	--++	2	-1	-1	1	1	V#2
13	-+-+	2	-1	1	-1	1	V#3
14	-++-	2	-1	1	1	-1	V#4
15	+--+	2	1	-1	-1	1	V#5
16	+-+-	2	1	-1	1	-1	V#6
17	++--	2	1	1	-1	-1	V#7
18	++++	2	1	1	1	1	V#8
19	0000	2	0	0	0	0	V#9
20	0000	2	0	0	0	0	V#10
21	-000	3	-1	0	0	0	
22	+000	3	1	0	0	0	
23	0-00	3	0	-1	0	0	
24	0+00	3	0	1	0	0	
25	00-0	3	0	0	-1	0	
26	00+0	3	0	0	1	0	
27	000-	3	0	0	0	-1	
28	000+	3	0	0	0	1	
29	0000	3	0	0	0	0	
30	0000	3	0	0	0	0	

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[a] Temperatures at 40, 55, and 70 °C; Organic Reagent = ~100, ~500, and ~2000 ppm; Hydroxide concentration = 0.5, 1.5, and 2.5 Molar; Copper(II) added as soluble $CuSO_4 \cdot 5H_2O$ solution = 0.1, 1, and 10 ppm.

[b] Test Vessel #'s for 3PB, 2PB and PBA data shown in Appendices D, E and F, respectively.

APPENDIX C

EXPERIMENTAL

Solutions were made from reagent grade chemicals. Aldrich Chemical Co. supplied triphenylboron, diphenylborinic acid ethanolamine ester and phenylboric acid. Note that the solid triphenylboron compound, not the 9 wt % 3PB·NaOH adduct in solution, was used as reagent 3PB chemical in this study. All chemicals were weighed on calibrated balances checked daily before use (Operating Procedure #IWT-OP-011). The weights used for balance checks were calibrated at the SRTC Standards Laboratory. Volume measurements were made with glassware whose accuracy has been verified by gravimetric methods using water as a standard (Operating Procedure #IWT-OP-009).

Samples were maintained at the specified testing temperatures by placement in laboratory ovens. Temperatures within the air-space of the ovens was determined by thermometers constantly kept in place within the ovens in very close proximity to the set of test vessels. Thermometers used were calibrated by SRTC Standards Laboratory using NIST-traceable procedures. Oven display temperature and thermometer temperatures were recorded on appropriate data sheets located at each oven. Upon completion of the tests, these temperature data sheets were kept as a permanent record in C. L. Crawford's Laboratory Notebook WSRC-NB-95-308. Temperature monitoring and control during normal laboratory hours was conducted by researchers and technicians. Temperatures were also recorded on night-shift and weekend-shifts by SRTC Control Room personnel.

Tests were carried out in 160 mL carbon-steel, air-sealed containers without constant stirring, i.e., as static systems. Containers were cleaned before testing by rinsing with deionized water, contacting with ~1% nitric acid for ~1 hr, rinsing with deionized water, heat treating at ~580 °C for at least 8 hrs, and finally soaking in 0.5 M NaOH for at least 8 hours.

The same test matrix for the initial set of samples with each organic component was used to readily evaluate each test series against the others (i.e., to determine the overall relative reactivities of 3PB, 2PB and PBA). The test matrix is statistically designed with the following parameters at the designated levels:

<u>Parameter</u>	<u>Levels</u>
Temperature	40, 55, and 70 °C
Organic Reagent	100, 500, and 2000 ppm
Hydroxide Concentration	0.5, 1.5, and 2.5 Molar
Copper(II)	0.1, 1, and 10 ppm

Copper was added as a soluble copper(II) sulfate ($CuSO_4 \cdot 5H_2O$) solution to each alkaline solution containing the dissolved organic reagent. Two vessels containing various amounts of the starting organic reagent and hydroxide ion were prepared without added copper and stored at room temperature. These two 'control samples' were prepared as an indication of the ambient temperature stability of the various organic components in air-sealed alkaline aqueous solution only.

Initial unreacted samples from all solutions were analyzed to provide starting measurements of components present. Subsequent sampling of the solutions were performed on a frequency of approximately once every 2-3 days up to ~ 500 hrs. Solutions were removed from the test temperatures and cooled to ambient temperatures by repetitive immersions in water baths prior to sampling. Solutions were mixed by vigorous shaking of the carbon-steel vessels immediately prior to gas-phase and solution sampling. All test-vessels containing the solution samples were weighed prior to and immediately after sampling in attempts to identify any significant evaporative losses during the tests. A typical sampling consisted of removing ≤ 0.5 cc gas from the vapor-space within the sealed vessel and approximately 4 mL solution (~ 1 mL analyzed for liquid benzene, ~2 mL for soluble organics analysis and ~1 mL for soluble boron analysis). The aqueous solution samples were not filtered prior to either soluble organics or boron analyses. No insoluble species were observed in any of the solutions studied. An appropriate amount of ambient air equal to the gas or liquid amount to be withdrawn was introduced into the sealed vessels immediately before each sampling to prevent depressurization of the sealed vessels due to multiple gas and solution sampling over the duration of the tests.

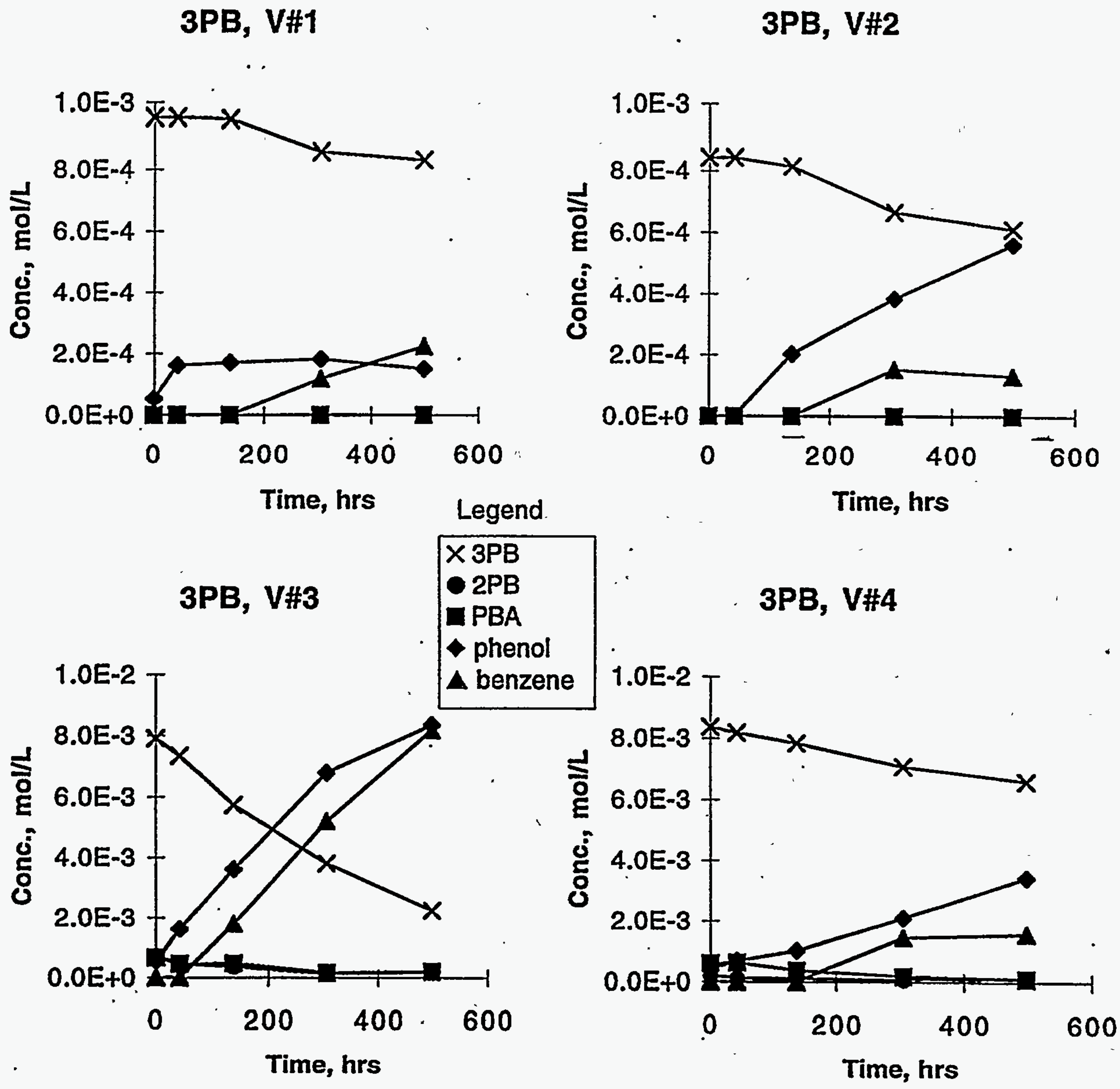
Organic components were measured by HPLC methods (Analytical Development Section, Analytical Operating Procedures Manual, L16.1). The two different HPLC methods employed were HPLC #1: (TPB^-, 3PB and 2PB Analysis) TSP LC, acetonitrile-ammonium phosphate buffer eluent, Whatman ODS-2 column (TPB^- retention ≈ 5.5 minutes, 3PB retention ≈ 11.5 minutes, 2PB retention ≈ 7.8 minutes) and HPLC #2: (PBA and Phenol Analysis) Hewlett Packard LC, acetonitrile-water eluent, Chemco-5-ODS column (PBA retention ≈ 10.5 minutes and phenol retention ≈ 14.6 minutes). Soluble boron analysis was obtained by ICP-ES. Due to recent questions arising from the boron analysis by ICP-ES in the presence of relatively large quantities of dissolved organics, boron data from present tests are being further analyzed before reporting.

Benzene was estimated from each of the reaction systems by subtracting the sum of all measured soluble organic decomposition products at each analysis time increment from the molar amount of measured starting organic species. Because no other significant organic products were observed in the HPLC chromatographs other than those reported in Appendices D-G, this calculated benzene estimation should give a conservative (maximum) amount of benzene produced in each test.

The actual amounts of benzene produced were estimated by gas chromatography (GC) measurements. The GC instruments was calibrated for benzene with gravimetrically prepared standards from reagent grade benzene (Operating Procedure #IWT-OP-007). Both gas-phase (from within the sealed carbon-steel vessels) and liquid-phase (from 0.25 - 0.5 mL aliquots of the alkaline aqueous solutions) benzene were measured. Gas-phase benzene measurements were estimated by transferring a known volume of gas from within the sealed carbon-steel vessels to a sealed 16 mL secondary container . Injections from the secondary container were made directly into the GC instrument. Liquid-phase benzene measurements were conducted by transferring a measured liquid aliquot of the alkaline aqueous solution into a sealed secondary container (typically 0.25-0.5 ml of solution into a 0.130 L glass bulb), agitating/swirling the glass bulb to ensure complete liquid 'coating' of the inner vessel walls to promote maximum liquid/vapor surface area within the bulb, and injection of a gas sample from the sealed bulb directly into the GC instrument. Final reacted samples from all of the tests were analyzed for soluble copper to determine the extent of copper solubility in the alkaline aqueous systems. The alkaline solutions were filtered with a 0.45 µm filter to remove any potential solid copper-containing species and acidified to pH ≤ 2 before submission to ADS for soluble copper concentrations determined by ICP-ES. Measurements of soluble copper were not available at the time of this report. These data will be reported at a later time.

Appendix D
Sample Data From 3PB Tests

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) 3PB
1	40	100-200	0.5	0.1	< 1.0E-06
2	40	100-200	2.5	10	< 1.0E-06
3	40	1500-2000	0.5	10	1.40E-05
4	40	1500-2000	2.5	0.1	4.50E-06

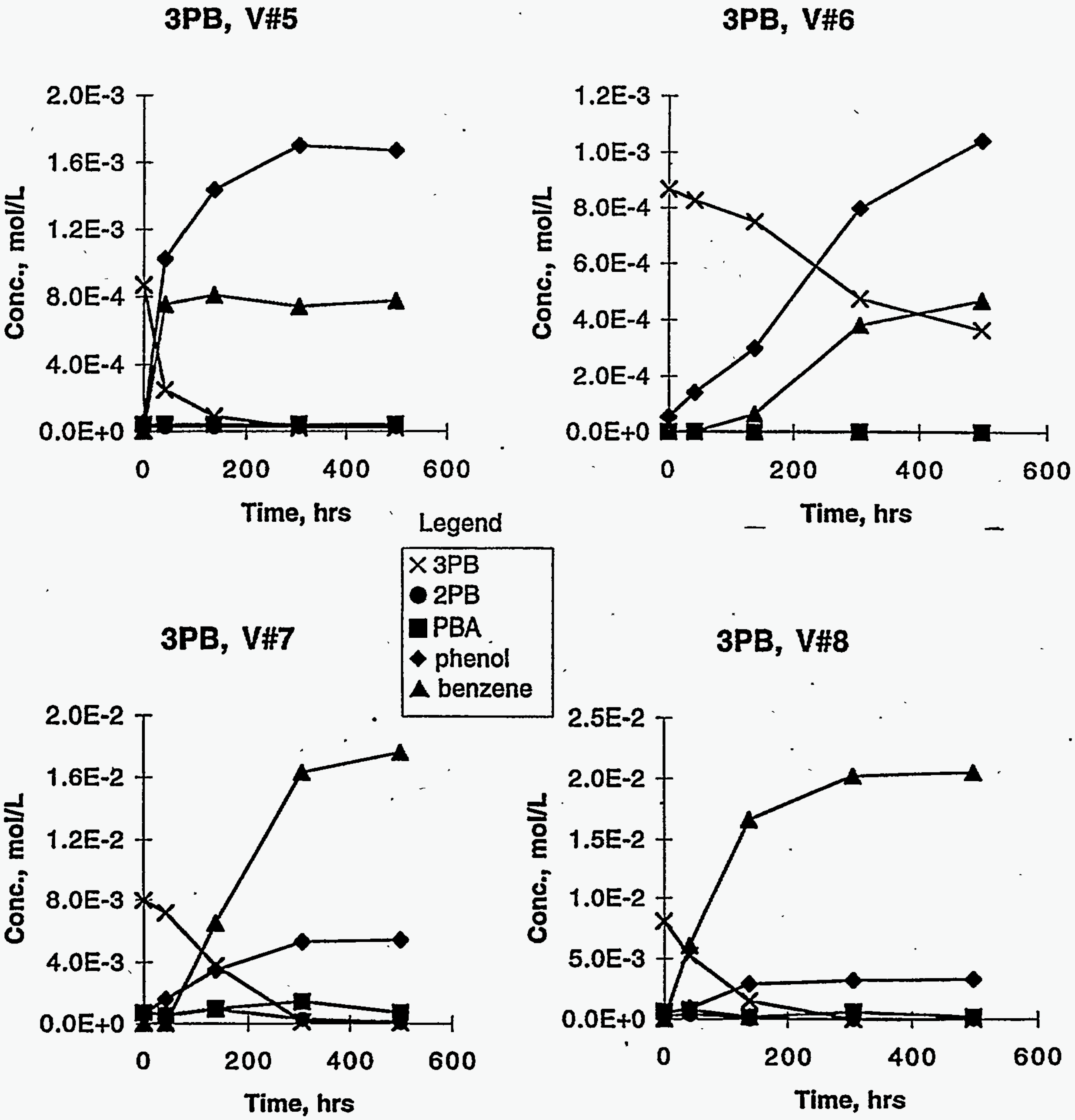

3PB, V#1

3PB, V#2

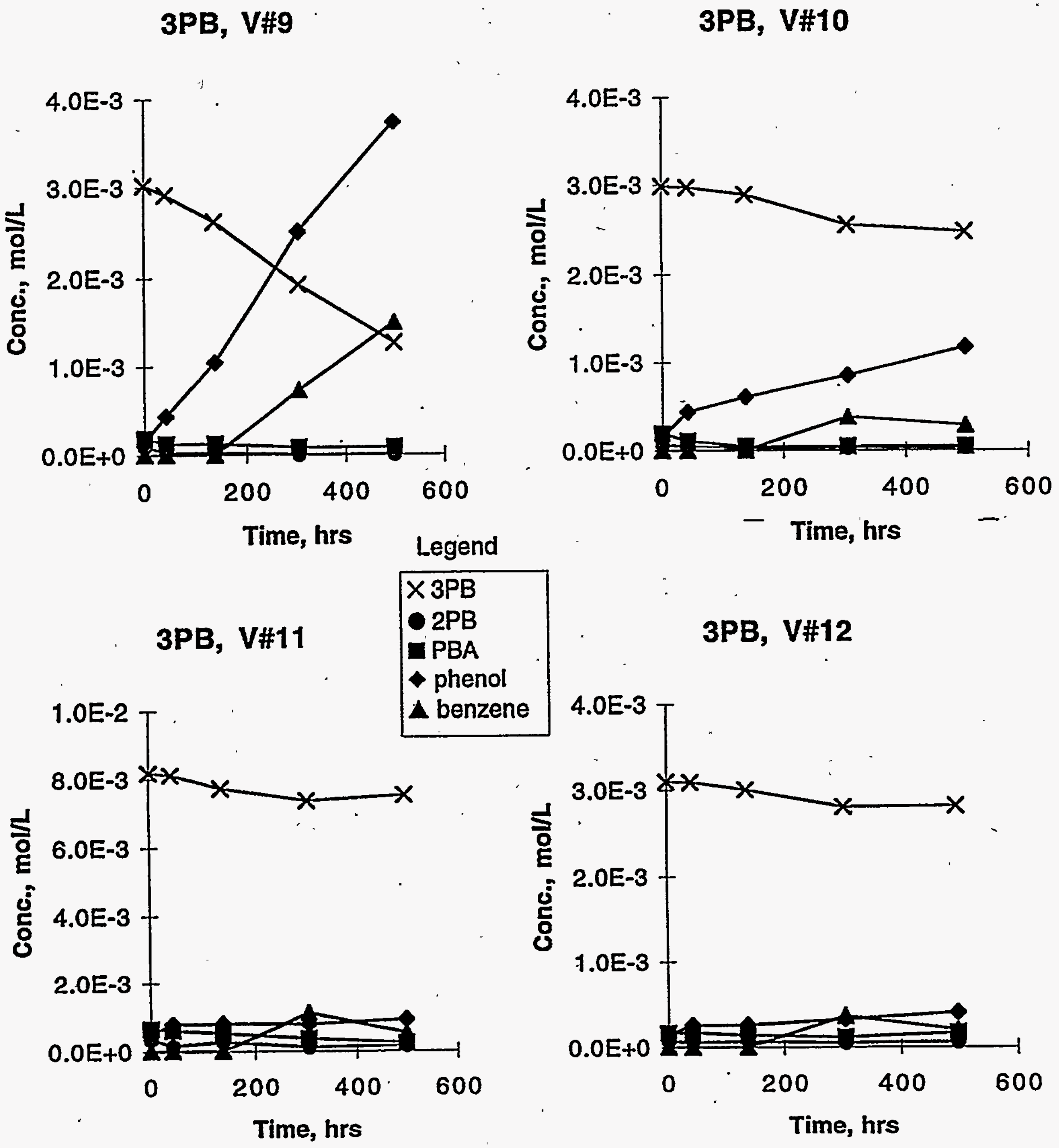
3PB, V#3

3PB, V#4

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) 3PB
5	70	100-200	0.5	10	1.50E-05
6	70	100-200	2.5	0.1	< 1.0E-06
7	70	1500-2000	0.5	0.1	2.00E-05
8	70	1500-2000	2.5	10	6.70E-05



Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) 3PB
9	55	400-700	1.5	1	2.60E-06
10	55	400-700	1.5	1	< 1.0E-06
11	23-25	1600-2000	1.5	NA	1.70E-06
12	23-25	400-700	1.5	NA	< 1.0E-06



Sample Data from 3PB Tests

Time (Hours)	V1 3PB (mg/L)	3PB (mole/L)	log(3PB)	d(3PB)/dt ((mole/L)/hr)	1st order k hr(-1)	2PB (mg/L)	2PB (mole/L)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	231	9.5E-4	-3.02E+00			0	0.0E+0	0	0.0E+0	5	5.3E-5	0.00E+00
42	231	9.5E-4	-3.02E+00	0.00E+00	0.00E+00	0	0.0E+0	0	0.0E+0	15	1.6E-4	0.00E+00
137.25	230	9.5E-4	-3.02E+00	3.01E-08	1.37E-05	0	0.0E+0	0	0.0E+0	16	1.7E-4	0.00E+00
305.5	207	8.5E-4	-3.07E+00	3.24E-07	1.56E-04	0	0.0E+0	0	0.0E+0	17	1.8E-4	1.16E-04
498.25	201	8.3E-4	-3.08E+00	2.49E-07	1.21E-04	0	0.0E+0	0	0.0E+0	14	1.5E-4	2.23E-04

220 = Average
15 =St.Dev.
7 =%RSD

Time Hours	V2 3PB (mg/L)	3PB (mole/L)	log(3PB)	((mol/L)/hr) d(3PB)/dt	1st order k hr(-1)	2PB (mg/L)	2PB (mole/L)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	204	8.4E-4	-3.07E+00			0	0.0E+0	0	0.0E+0	0	0.0E+0	0.00E+00
42	204	8.4E-4	-3.07E+00	0.00E+00	0.00E+00	0	0.0E+0	0	0.0E+0	0	0.0E+0	0.00E+00
137.25	197	8.1E-4	-3.09E+00	2.11E-07	1.10E-04	0	0.0E+0	0	0.0E+0	19	2.0E-4	0.00E+00
305.5	161	6.6E-4	-3.18E+00	5.81E-07	3.37E-04	0	0.0E+0	0	0.0E+0	36	3.8E-4	1.50E-04
498.25	148	6.1E-4	-3.21E+00	4.64E-07	2.80E-04	0	0.0E+0	0	0.0E+0	53	5.6E-4	1.30E-04

183 = Average
26 =St.Dev.
14 =%RSD

Time Hours	V3 3PB (mg/L)	3PB (mole/L)	log(3PB)	((mol/L)/hr) d(3PB)/dt	1st order k hr(-1)	2PB (mg/L)	2PB (mole/L)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1916	7.9E-3	-2.10E+00			133	7.4E-4	80	6.6E-4	50	5.3E-4	0.00E+00
42	1777	7.3E-3	-2.13E+00	1.37E-05	7.79E-04	81	4.5E-4	53	4.3E-4	151	1.6E-3	0.00E+00
137.25	1388	5.7E-3	-2.24E+00	1.59E-05	1.02E-03	63	3.5E-4	56	4.6E-4	338	3.6E-3	1.79E-03
305.5	918	3.8E-3	-2.42E+00	1.35E-05	1.05E-03	22	1.2E-4	19	1.6E-4	637	6.8E-3	5.19E-03
498.25	538	2.2E-3	-2.65E+00	1.14E-05	1.11E-03	32	1.8E-4	23	1.9E-4	785	8.4E-3	8.18E-03

1307 = Average
579 =St.Dev.
44 =%RSD

Time Hours	V4 3PB (mg/L)	3PB (mole/L)	log(3PB)	((mol/L)/hr) d(3PB)/dt	1st order k hr(-1)	2PB (mg/L)	2PB (mole/L)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	2023	8.4E-3	-2.08E+00			36	2.0E-4	71	5.8E-4	39	4.1E-4	0.00E+00
42	1977	8.2E-3	-2.09E+00	4.52E-06	2.38E-04	22	1.2E-4	75	6.2E-4	63	6.7E-4	0.00E+00
137.25	1896	7.8E-3	-2.11E+00	3.82E-06	2.05E-04	18	1.0E-4	45	3.7E-4	95	1.0E-3	0.00E+00
305.5	1711	7.1E-3	-2.15E+00	4.22E-06	2.38E-04	14	7.7E-5	21	1.7E-4	197	2.1E-3	1.44E-03
498.25	1598	6.6E-3	-2.18E+00	3.52E-06	2.06E-04	16	8.8E-5	12	9.8E-5	323	3.4E-3	1.55E-03

1841 = Average
181 =St.Dev.
10 =%RSD

Time Hours	V5 3PB (mg/L)	3PB (mole/L)	log(3PB)	((mol/L)/hr) d(3PB)/dt	1st order k hr(-1)	2PB (mg/L)	2PB (mole/L)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	210	8.7E-4	-3.06E+00			5	2.8E-5	5	4.1E-5	5	5.3E-5	0.00E+00
42	59	2.4E-4	-3.61E+00	1.48E-05	1.31E-02	5	2.8E-5	5	4.1E-5	96	1.0E-3	7.53E-04
137.25	21	8.7E-5	-4.06E+00	5.69E-06	7.29E-03	5	2.8E-5	5	4.1E-5	135	1.4E-3	8.09E-04
305.5	5	2.1E-5	-4.69E+00	2.77E-06	5.31E-03	5	2.8E-5	5	4.1E-5	160	1.7E-3	7.41E-04
498.25	5	2.1E-5	-4.69E+00	1.70E-06	3.26E-03	5	2.8E-5	5	4.1E-5	157	1.7E-3	7.73E-04

60 = Average
87 =St.Dev.
145 =%RSD

Time	V6 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	210	8.7E-4	-3.06E+00			0	0.0E+0	0	0.0E+0	5	5.3E-5	0.00E+00
42	200	8.3E-4	-3.08E+00	9.83E-07	5.05E-04	0	0.0E+0	0	0.0E+0	13	1.4E-4	0.00E+00
137.25	181	7.5E-4	-3.13E+00	8.73E-07	4.70E-04	0	0.0E+0	0	0.0E+0	28	3.0E-4	6.14E-05
305.5	115	4.7E-4	-3.32E+00	1.28E-06	8.56E-04	0	0.0E+0	0	0.0E+0	75	8.0E-4	3.79E-04
498.25	88	3.6E-4	-3.44E+00	1.01E-06	7.58E-04	0	0.0E+0	0	0.0E+0	98	1.0E-3	4.69E-04

159 = Average
54 =St.Dev.
34 =%RSD

Time	V7 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	1929	8.0E-3	-2.10E+00			145	8.0E-4	84	6.9E-4	60	6.4E-4	0.00E+00
42	1726	7.1E-3	-2.15E+00	2.00E-05	1.15E-03	90	5.0E-4	65	5.3E-4	146	1.6E-3	0.00E+00
137.25	906	3.7E-3	-2.43E+00	3.08E-05	2.39E-03	164	9.1E-4	113	9.3E-4	325	3.5E-3	6.48E-03
305.5	28	1.2E-4	-3.93E+00	2.57E-05	6.00E-03	50	2.8E-4	170	1.4E-3	497	5.3E-3	1.63E-02
498.25	7	2.9E-5	-4.54E+00	1.59E-05	4.90E-03	10	5.5E-5	83	6.8E-4	507	5.4E-3	1.76E-02

919 = Average
908 =St.Dev.
99 =%RSD

Time	V8 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	1950	8.1E-3	-2.09E+00			38	2.1E-4	73	6.0E-4	41	4.4E-4	0.00E+00
42	1264	5.2E-3	-2.28E+00	6.74E-05	4.48E-03	77	4.3E-4	87	7.1E-4	83	8.8E-4	6.05E-03
137.25	358	1.5E-3	-2.83E+00	4.79E-05	5.36E-03	10	5.5E-5	20	1.6E-4	270	2.9E-3	1.66E-02
305.5	5	2.1E-5	-4.69E+00	2.63E-05	8.48E-03	7	3.9E-5	74	6.1E-4	301	3.2E-3	2.02E-02
498.25	5	2.1E-5	-4.69E+00	1.61E-05	5.20E-03	10	5.5E-5	20	1.6E-4	309	3.3E-3	2.05E-02

716 = Average
861 =St.Dev.
120 =%RSD

Time	V9 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	731	3.0E-3	-2.52E+00			17	9.4E-5	23	1.9E-4	14	1.5E-4	0.00E+00
42	705	2.9E-3	-2.54E+00	2.56E-06	3.74E-04	5	2.8E-5	15	1.2E-4	41	4.4E-4	0.00E+00
137.25	633	2.6E-3	-2.58E+00	2.95E-06	4.55E-04	5	2.8E-5	15	1.2E-4	98	1.0E-3	0.00E+00
305.5	464	1.9E-3	-2.72E+00	3.61E-06	6.46E-04	0	0.0E+0	10	8.2E-5	235	2.5E-3	7.26E-04
498.25	304	1.3E-3	-2.90E+00	3.54E-06	7.65E-04	0	0.0E+0	10	8.2E-5	350	3.7E-3	1.48E-03

567 = Average
180 =St.Dev.
32 =%RSD

Time	V10 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	722	3.0E-3	-2.53E+00			11	6.1E-5	24	2.0E-4	15	1.6E-4	0.00E+00
42	719	3.0E-3	-2.53E+00	2.95E-07	4.31E-05	9	5.0E-5	13	1.1E-4	41	4.4E-4	0.00E+00
137.25	699	2.9E-3	-2.54E+00	6.92E-07	1.02E-04	5	2.8E-5	5	4.1E-5	57	6.1E-4	0.00E+00
305.5	615	2.5E-3	-2.60E+00	1.45E-06	2.28E-04	5	2.8E-5	5	4.1E-5	80	8.5E-4	3.78E-04
498.25	598	2.5E-3	-2.61E+00	1.03E-06	1.64E-04	4	2.2E-5	5	4.1E-5	110	1.2E-3	2.81E-04

671 = Average
59 =St.Dev.
9 =%RSD

Time	V11 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	1980	8.2E-3	-2.09E+00			63	3.5E-4	80	6.6E-4	50	5.3E-4	0.00E+00
42	1963	8.1E-3	-2.09E+00	1.67E-06	8.92E-05	29	1.6E-4	75	6.2E-4	74	7.9E-4	0.00E+00
137.25	1867	7.7E-3	-2.11E+00	3.40E-06	1.86E-04	49	2.7E-4	65	5.3E-4	75	8.0E-4	0.00E+00
305.5	1780	7.4E-3	-2.13E+00	2.70E-06	1.51E-04	21	1.2E-4	44	3.6E-4	74	7.9E-4	1.10E-03
498.25	1819	7.5E-3	-2.12E+00	1.33E-06	7,39E-05	28	1.6E-4	30	2.5E-4	86	9.1E-4	5.24E-04

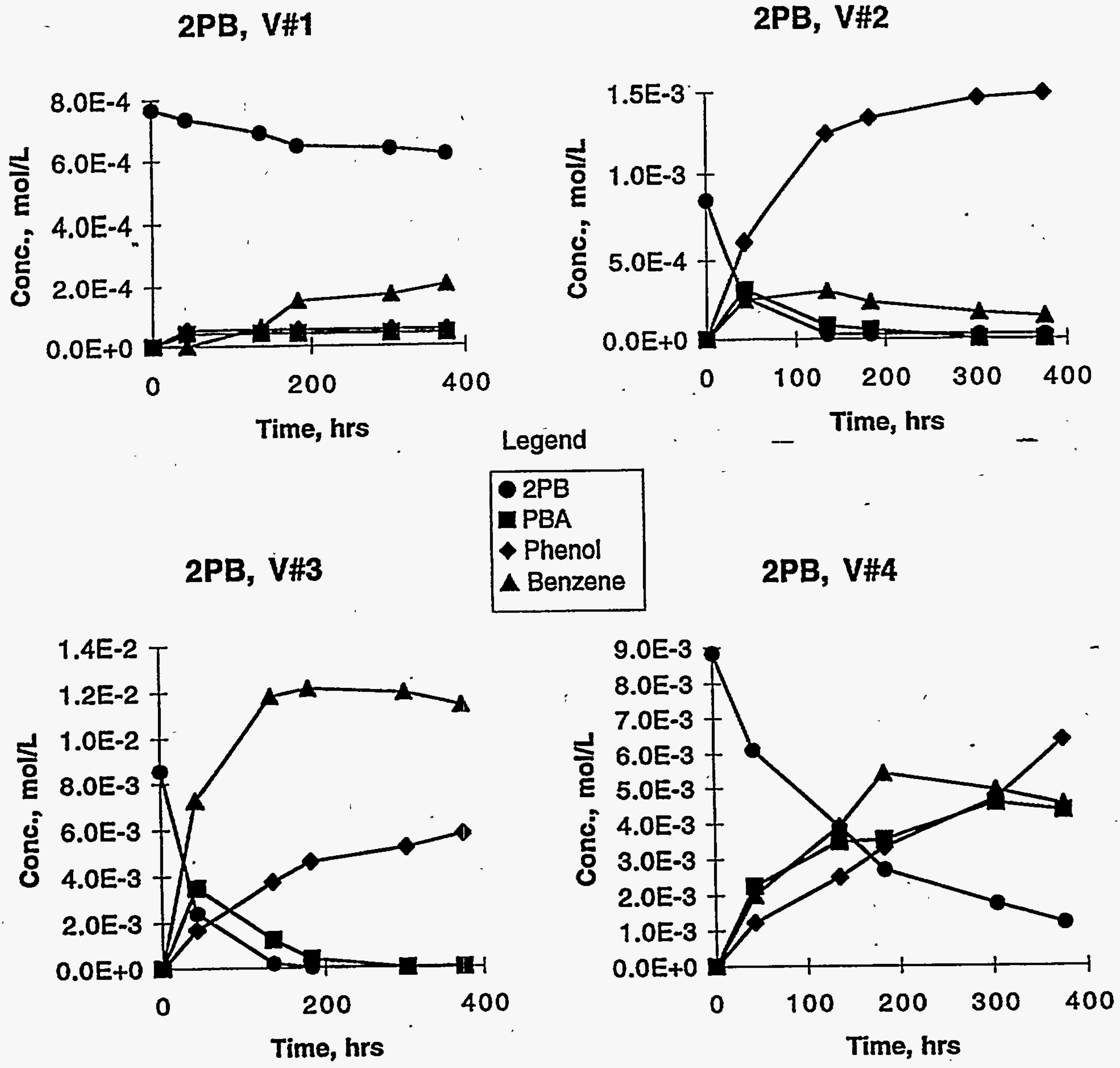
1862 = Average
88 =St.Dev.
5 =%RSD

Time	V12 3PB	3PB	log(3PB)	((mol/L)/hr)	1st order k	2PB	2PB	PBA	PBA	Phenol	Phenol	Calculated Benzene
Hours	(mg/L)	(mole/L)		d(3PB)/dt	hr(-1)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mg/L)	(mole/L)	(mole/L)
0	750	3.1E-3	-2.51E+00			13	7.2E-5	20	1.6E-4	14	1.5E-4	0.00E+00
42	749	3.1E-3	-2.51E+00	9.63E-08	1.38E-05	10	5.5E-5	21	1.7E-4	24	2.6E-4	0.00E+00
137.25	727	3.0E-3	-2.52E+00	6.92E-07	9.86E-05	11	6.1E-5	17	1.4E-4	24	2.6E-4	0.00E+00
305.5	678	2.8E-3	-2.55E+00	9.73E-07	1.43E-04	9	5.0E-5	14	1.1E-4	30	3.2E-4	3.58E-04
498.25	680	2.8E-3	-2.55E+00	5.80E-07	8.54E-05	10	5.5E-5	20	1.6E-4	37	3.9E-4	1.99E-04

717 = Average
36 =St.Dev.
5 =%RSD

Appendix E
Sample Data From 2PB Tests

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) 2PB
1	40	100-200	0.5	0.1	< 1.0E-06
2	40	100-200	2.5	10	1.40E-05
3	40	1500-2000	0.5	10	1.50E-04
4	40	1500-2000	2.5	0.1	6.40E-05



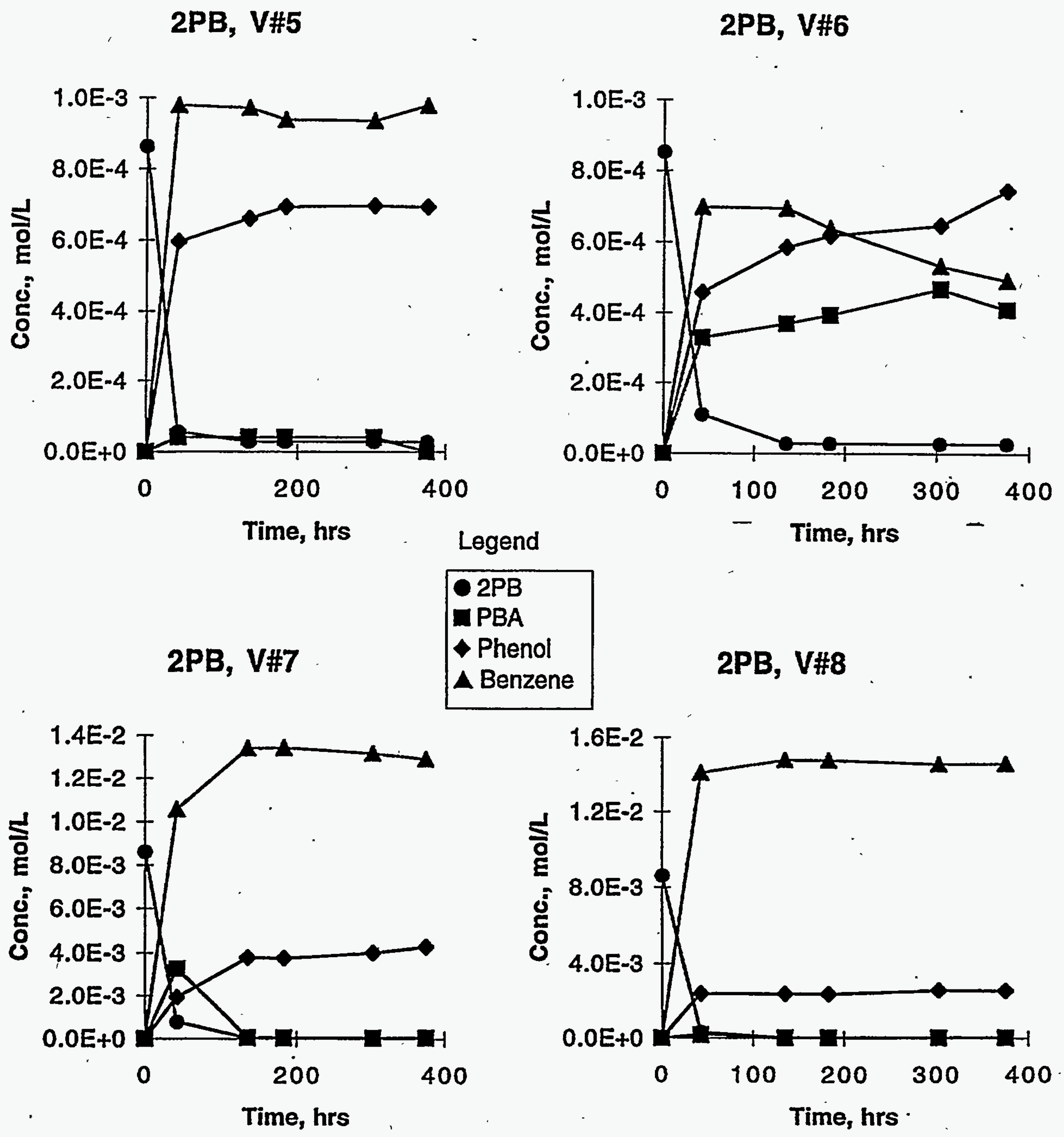
2PB, V#1

2PB, V#2

2PB, V#3

2PB, V#4

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) 2PB
5	70	100-200	0.5	10	≥ 2.0E-05
6	70	100-200	2.5	0.1	≥ 1.9E-05
7	70	1500-2000	0.5	0.1	1.90E-04
8	70	1500-2000	2.5	10	2.00E-04

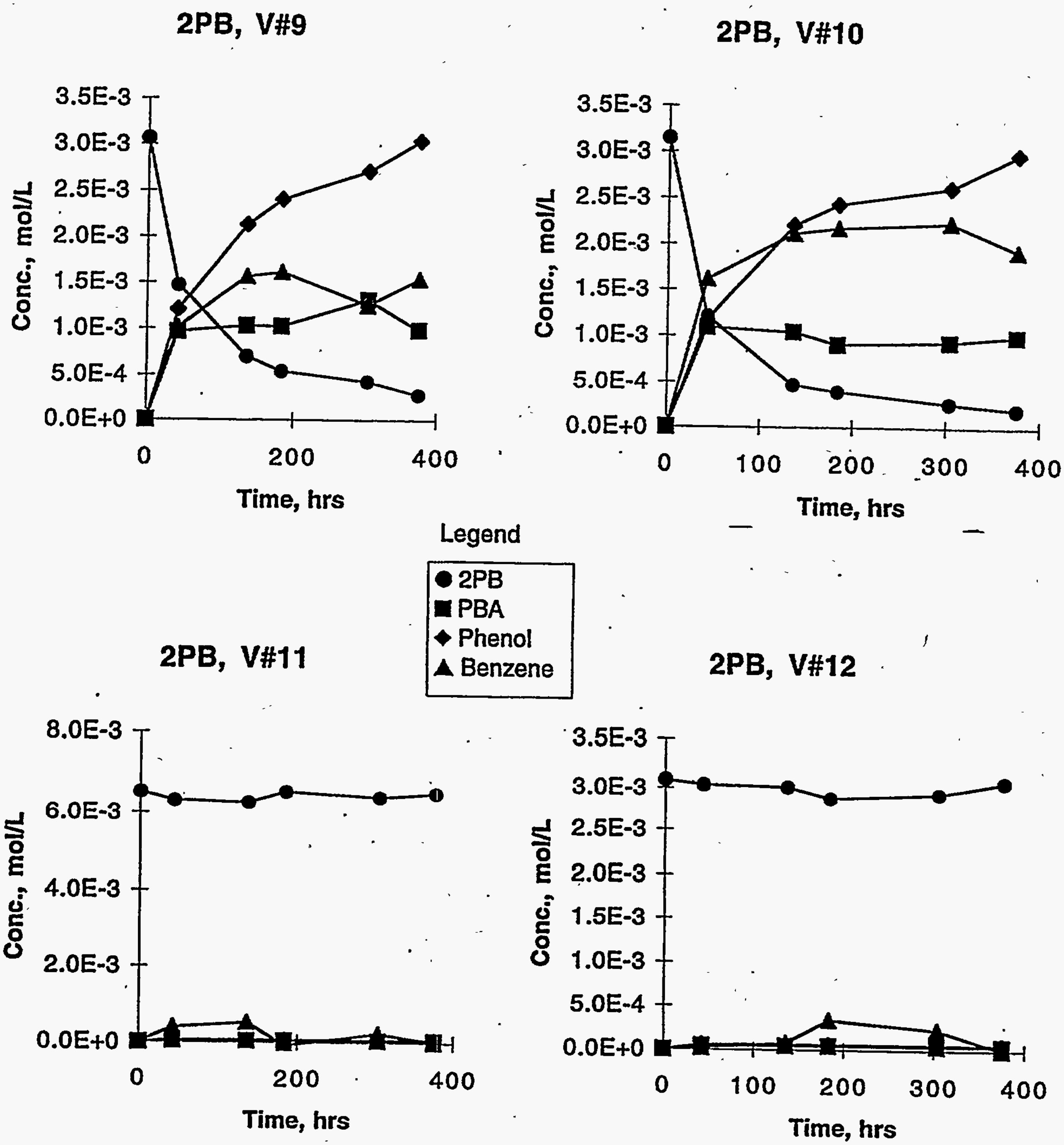

2PB, V#5

2PB, V#6

2PB, V#7

2PB, V#8

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) 2PB
9	55	400-700	1.5	1	3.70E-05
10	55	400-700	1.5	1	4.60E-05
11	23-25	1600-2000	1.5	NA	5.70E-06
12	23-25	400-700	1.5	NA	1.30E-06



Sample Data from 2PB Tests

Time (Hours)	V1 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	139	7.7E-4	-3.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	133	7.4E-4	-3.1E+0	7.8E-7	4.5E-4	5	4.10E-05	5	5.32E-05	0.00E+00
135.5	125	6.9E-4	-3.2E+0	5.7E-7	3.4E-4	5	4.10E-05	5	5.32E-05	6.07E-05
183.5	117	6.5E-4	-3.2E+0	6.6E-7	4.1E-4	5	4.10E-05	5	5.32E-05	1.49E-04
303.5	115	6.4E-4	-3.2E+0	4.3E-7	2.7E-4	5	4.10E-05	5	5.32E-05	1.70E-04
375.5	112	6.2E-4	-3.2E+0	4.0E-7	2.5E-4	5	4.10E-05	5	5.32E-05	2.05E-04

124 = Average
11 =St. dev.
9 =%RSD

Time (Hours)	V2 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	152	8.4E-4	-3.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	47	2.6E-4	-3.6E+0	1.4E-5	1.2E-2	38	3.12E-04	57	6.06E-04	2.43E-04
135.5	5	2.8E-5	-4.6E+0	6.0E-6	1.1E-2	10	8.20E-05	117	1.24E-03	2.99E-04
183.5	5	2.8E-5	-4.6E+0	4.4E-6	8.1E-3	7	5.74E-05	126	1.34E-03	2.28E-04
303.5	5	2.8E-5	-4.6E+0	2.7E-6	4.9E-3	0	0.00E+00	137	1.46E-03	1.64E-04
375.5	5	2.8E-5	-4.6E+0	2.2E-6	3.9E-3	0	0.00E+00	140	1.49E-03	1.37E-04

37 = Average
59 =St. dev.
162 =%RSD

Time (Hours)	V3 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1553	8.6E-3	-2.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	432	2.4E-3	-2.6E+0	1.5E-4	1.3E-2	423	3.47E-03	158	1.68E-03	7.25E-03
135.5	37	2.0E-4	-3.7E+0	6.2E-5	1.2E-2	151	1.24E-03	350	3.72E-03	1.18E-02
183.5	5	2.8E-5	-4.6E+0	4.7E-5	1.4E-2	47	3.85E-04	431	4.59E-03	1.22E-02
303.5	5	2.8E-5	-4.6E+0	2.8E-5	8.2E-3	0	0.00E+00	485	5.16E-03	1.20E-02
375.5	5	2.8E-5	-4.6E+0	2.3E-5	6.6E-3	0	0.00E+00	540	5.74E-03	1.14E-02

340 = Average
618 =St. dev.
182 =%RSD

Time (Hours)	V4 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1598	8.8E-3	-2.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	1103	6.1E-3	-2.2E+0	6.4E-5	3.8E-3	274	2.25E-03	115	1.22E-03	2.01E-03
135.5	705	3.9E-3	-2.4E+0	3.6E-5	2.6E-3	425	3.49E-03	235	2.50E-03	3.89E-03
183.5	488	2.7E-3	-2.6E+0	3.3E-5	2.8E-3	431	3.53E-03	312	3.32E-03	5.42E-03
303.5	316	1.7E-3	-2.8E+0	2.3E-5	2.3E-3	557	4.57E-03	440	4.68E-03	4.93E-03
375.5	219	1.2E-3	-2.9E+0	2.0E-5	2.3E-3	530	4.35E-03	600	6.38E-03	4.52E-03

738 = Average
526 =St. dev.
71 =%RSD

Time (Hours)	V5 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	156	8.6E-4	-3.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	10	5.5E-5	-4.3E+0	1.9E-5	2.8E-2	5	4.10E-05	56	5.96E-04	9.78E-04
135.5	5	2.8E-5	-4.6E+0	6.2E-6	1.1E-2	5	4.10E-05	62	6.60E-04	9.70E-04
183.5	5	2.8E-5	-4.6E+0	4.6E-6	8.1E-3	5	4.10E-05	65	6.91E-04	9.38E-04
303.5	5	2.8E-5	-4.6E+0	2.8E-6	4.9E-3	5	4.10E-05	65	6.95E-04	9.34E-04
375.5	5	2.8E-5	-4.6E+0	2.2E-6	4.0E-3	0	0.00E+00	65	6.91E-04	9.79E-04

31 = Average
61 =St. dev.
198 =%RSD

Time (Hours)	V6 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	154	8.5E-4	-3.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	20	1.1E-4	-4.0E+0	1.7E-5	2.1E-2	40	3.28E-04	43	4.57E-04	6.97E-04
135.5	5	2.8E-5	-4.6E+0	6.1E-6	1.1E-2	45	3.69E-04	55	5.85E-04	6.94E-04
183.5	5	2.8E-5	-4.6E+0	4.5E-6	8.1E-3	48	3.94E-04	58	6.17E-04	6.38E-04
303.5	5	2.8E-5	-4.6E+0	2.7E-6	4.9E-3	57	4.68E-04	61	6.47E-04	5.34E-04
375.5	5	2.8E-5	-4.6E+0	2.2E-6	4.0E-3	50	4.10E-04	70	7.45E-04	4.93E-04

32 = Average
60 =St. dev.
185 =%RSD

Time (Hours)	V7 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1562	8.6E-3	-2.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	139	7.7E-4	-3.1E+0	1.9E-4	2.5E-2	398	3.26E-03	181	1.93E-03	1.06E-02
135.5	5	2.8E-5	-4.6E+0	6.4E-5	1.8E-2	5	4.10E-05	355	3.78E-03	1.34E-02
183.5	5	2.8E-5	-4.6E+0	4.7E-5	1.4E-2	5	4.10E-05	354	3.77E-03	1.34E-02
303.5	5	2.8E-5	-4.6E+0	2.8E-5	8.2E-3	5	4.10E-05	377	4.01E-03	1.32E-02
375.5	5	2.8E-5	-4.6E+0	2.3E-5	6.6E-3	5	4.10E-05	402	4.27E-03	1.29E-02

287 = Average
627 =St. dev.
219 =%RSD

Time (Hours)	V8 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1560	8.6E-3	-2.1E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	56	3.1E-4	-3.5E+0	2.0E-4	3.4E-2	22	1.80E-04	222	2.36E-03	1.41E-02
135.5	5	2.8E-5	-4.6E+0	6.3E-5	1.8E-2	5	4.10E-05	221	2.35E-03	1.48E-02
183.5	5	2.8E-5	-4.6E+0	4.7E-5	1.4E-2	5	4.10E-05	222	2.36E-03	1.48E-02
303.5	5	2.8E-5	-4.6E+0	2.8E-5	8.2E-3	5	4.10E-05	240	2.55E-03	1.46E-02
375.5	5	2.8E-5	-4.6E+0	2.3E-5	6.6E-3	5	4.10E-05	237	2.52E-03	1.46E-02

273 = Average
631 =St. dev.
231 =%RSD

Time (Hours)	V9 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	554	3.1E-3	-2.5E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	266	1.5E-3	-2.8E+0	3.7E-5	7.5E-3	118	9.68E-04	113	1.20E-03	1.02E-03
135.5	127	7.0E-4	-3.2E+0	1.7E-5	4.7E-3	126	1.03E-03	200	2.13E-03	1.57E-03
183.5	98	5.4E-4	-3.3E+0	1.4E-5	4.1E-3	125	1.03E-03	226	2.40E-03	1.61E-03
303.5	78	4.3E-4	-3.4E+0	8.7E-6	2.8E-3	160	1.31E-03	255	2.71E-03	1.25E-03
375.5	50	2.8E-4	-3.6E+0	7.4E-6	2.8E-3	121	9.92E-04	286	3.04E-03	1.54E-03

195 = Average
191 =St. dev.
98 =%RSD

Time (Hours)	V.10 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	569	3.1E-3	-2.5E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	219	1.2E-3	-2.9E+0	4.6E-5	9.8E-3	133	1.09E-03	110	1.17E-03	1.61E-03
135.5	85	4.7E-4	-3.3E+0	2.0E-5	6.1E-3	127	1.04E-03	207	2.20E-03	2.11E-03
183.5	71	3.9E-4	-3.4E+0	1.5E-5	4.9E-3	111	9.10E-04	228	2.43E-03	2.17E-03
303.5	47	2.6E-4	-3.6E+0	9.5E-6	3.6E-3	114	9.39E-04	245	2.61E-03	2.23E-03
375.5	35	1.9E-4	-3.7E+0	7.9E-6	3.2E-3	122	1.00E-03	280	2.98E-03	1.93E-03

171 = Average
206 =St. dev.
120 =%RSD

Time (Hours)	V11 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1189	6.6E-3	-2.2E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	1145	6.3E-3	-2.2E+0	5.7E-6	3.9E-4	5	4.10E-05	5	5.32E-05	3.93E-04
135.5	1134	6.3E-3	-2.2E+0	2.2E-6	1.5E-4	5	4.10E-05	5	5.32E-05	5.14E-04
183.5	1188	6.6E-3	-2.2E+0	3.0E-8	2.0E-6	5	4.10E-05	5	5.32E-05	-8.31E-05
303.5	1160	6.4E-3	-2.2E+0	5.3E-7	3.5E-5	5	4.10E-05	5	5.32E-05	2.27E-04
375.5	1180	6.5E-3	-2.2E+0	1.3E-7	8.8E-6	5	4.10E-05	5	5.32E-05	5.36E-06

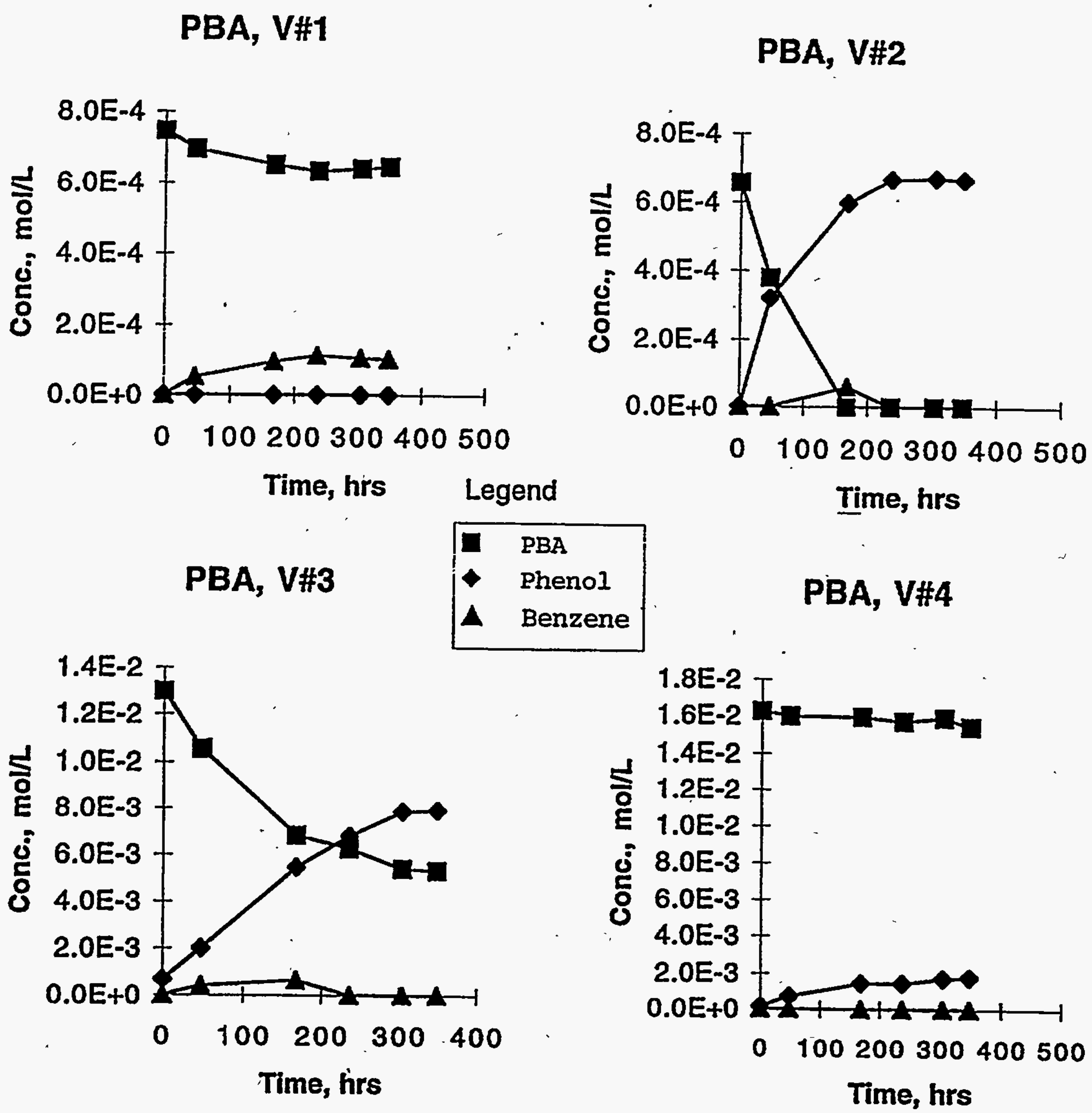
1166 = Average
23 =St. dev.
2 =%RSD

Time (Hours)	V12 2PB (mg/L)	2PB (mole/L)	log(2PB)	d(2PB)/dt (mole/L)/hr	1st order k hr(-1)	PBA (mg/L)	PBA (mole/L)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	559	3.1E-3	-2.5E+0			0	0.00E+00	0	0.00E+00	0.00E+00
42.5	549	3.0E-3	-2.5E+0	1.3E-6	1.8E-4	5	4.10E-05	5	5.32E-05	1.64E-05
135.5	544	3.0E-3	-2.5E+0	6.3E-7	8.9E-5	5	4.10E-05	5	5.32E-05	7.60E-05
183.5	520	2.9E-3	-2.5E+0	1.2E-6	1.7E-4	5	4.10E-05	5	5.32E-05	3.37E-04
303.5	530	2.9E-3	-2.5E+0	5.3E-7	7.6E-5	5	4.10E-05	5	5.32E-05	2.27E-04
375.5	555	3.1E-3	-2.5E+0	6.3E-8	8.8E-6	5	4.10E-05	5	5.32E-05	0.00E+00

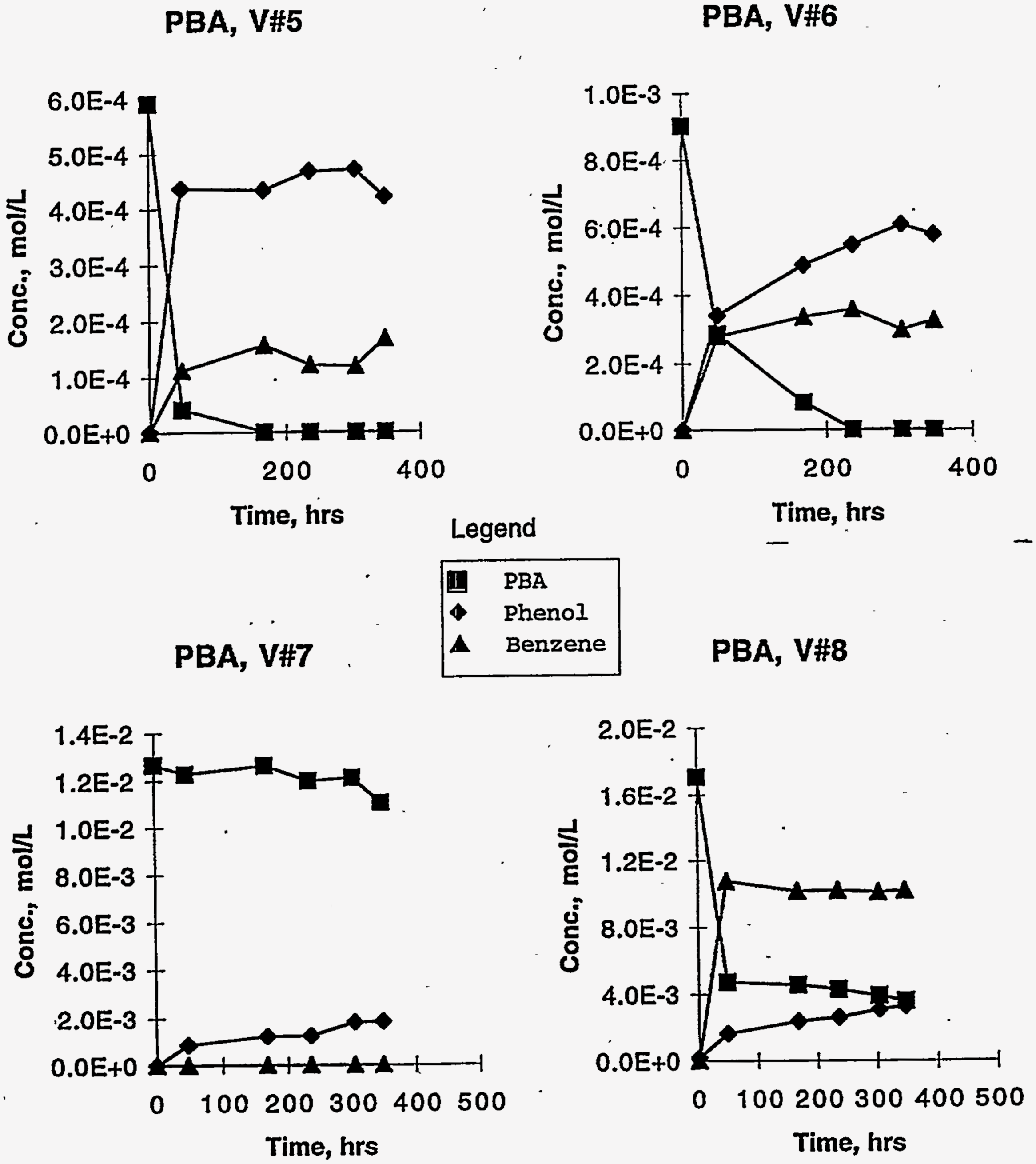
543 = Average
15 =St. dev.
3 =%RSD

Appendix F
Sample Data From PBA Tests

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) PBA
1	40	100-200	0.5	0.1	< 1.0E-06
2	40	100-200	2.5	10	5.30E-06
3	40	1500-2000	0.5	10	5.10E-05
4	40	1500-2000	2.5	0.1	5.10E-06



Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) PBA
5	70	100-200	0.5	10	≥5.8E-06
6	70	100-200	2.5	0.1	1.30E-05
7	70	1500-2000	0.5	0.1	7.60E-06
8	70	1500-2000	2.5	10	2.60E-04

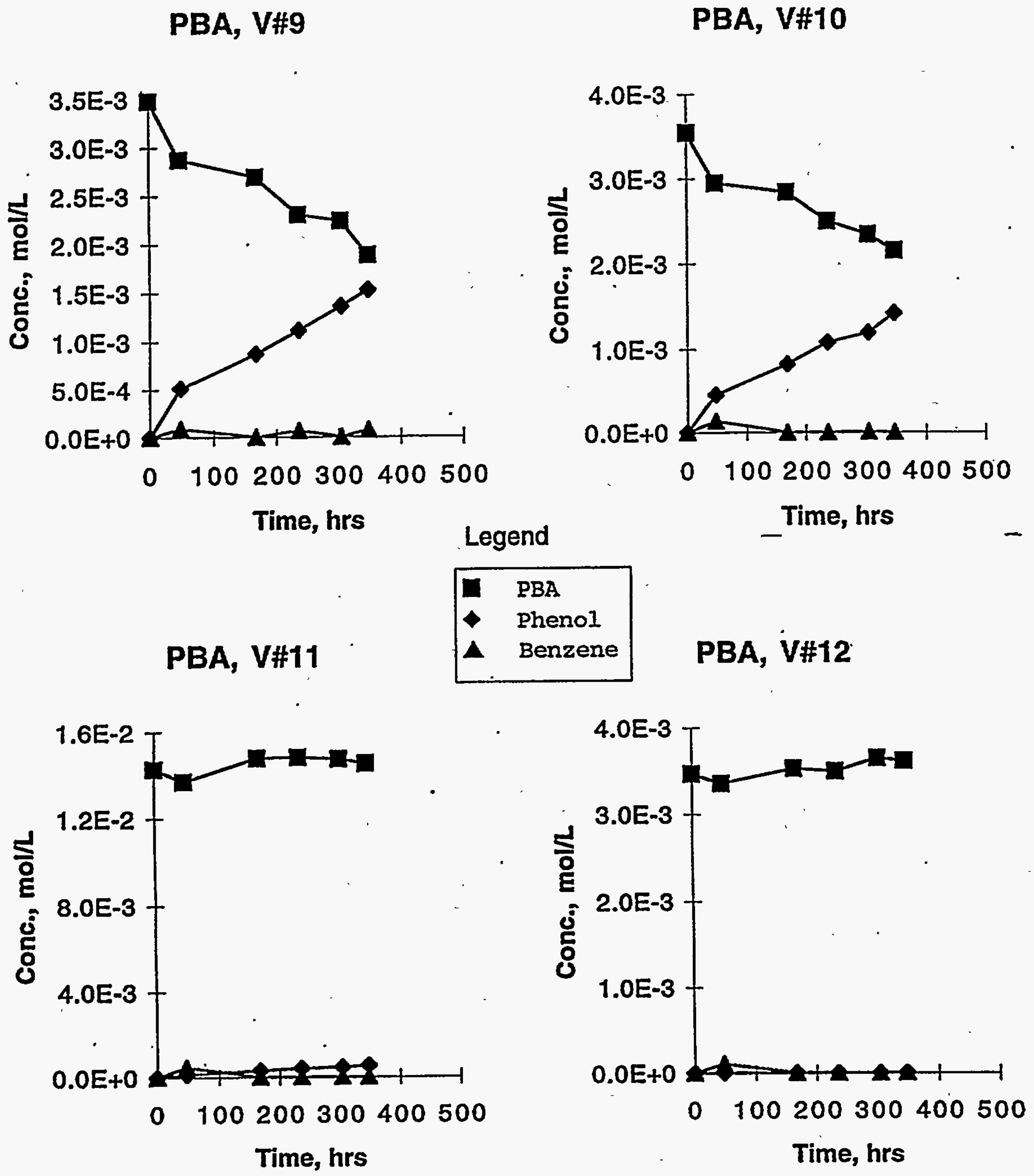

PBA, V#5

PBA, V#6

PBA, V#7

PBA, V#8

Vessel#	Temperature (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Initial Rate (mole/L/hr) PBA
9	55	400-700	1.5	1	1.00E-05
10	55	400-700	1.5	1	1.10E-05
11	23-25	1600-2000	1.5	NA	1.20E-06
12	23-25	400-700	1.5	NA	< 1.0E-06


PBA, V#9

PBA, V#10

PBA, V#11

PBA, V#12

Sample Data from PBA Tests

Time (Hours)	V1 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	91	7.5E-4	-3.1E+0			0	0.00E+00	0.00E+00
48	85	6.9E-4	-3.2E+0	1.1E-06	6.5E-04	0	0.00E+00	5.15E-05
168	79	6.5E-4	-3.2E+0	5.7E-07	3.5E-04	0	0.00E+00	9.57E-05
236	77	6.3E-4	-3.2E+0	4.8E-07	3.0E-04	0	0.00E+00	1.13E-04
304	78	6.4E-4	-3.2E+0	3.5E-07	2.2E-04	0	0.00E+00	1.06E-04
348	79	6.4E-4	-3.2E+0	2.9E-07	1.8E-04	0	0.00E+00	1.02E-04

81 = Average
5 = St.Dev.
7 =%RSD

Time (Hours)	V2 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	80	6.56E-04	-3.2E+00			0	0.00E+00	0.00E+00
48	46	3.77E-04	-3.4E+00	5.8E-06	5.0E-03	30	3.19E-04	0.00E+00
168	0	0.00E+00	#NUM!	3.9E-06	#NUM!	56	5.96E-04	5.92E-05
236	0	0.00E+00	#NUM!	2.8E-06	#NUM!	63	6.68E-04	0.00E+00
304	0	0.00E+00	#NUM!	2.2E-06	#NUM!	63	6.70E-04	0.00E+00
348	0	0.00E+00	#NUM!	1.9E-06	#NUM!	63	6.67E-04	0.00E+00

21 = Average
34 = St.Dev.
163 =%RSD

Time (Hours)	V3 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1583	1.3E-2	-1.9E+0			64	6.85E-04	0.00E+00
48	1286	1.1E-2	-2.0E+0	5.1E-05	1.9E-03	190	2.02E-03	4.19E-04
168	833	6.8E-3	-2.2E+0	3.7E-05	1.7E-03	515	5.48E-03	6.66E-04
236	765	6.3E-3	-2.2E+0	2.8E-05	1.3E-03	640	6.81E-03	0.00E+00
304	663	5.4E-3	-2.3E+0	2.5E-05	1.2E-03	739	7.86E-03	0.00E+00
348	653	5.4E-3	-2.3E+0	2.2E-05	1.1E-03	744	7.92E-03	0.00E+00

964 = Average
382 = St.Dev.
40 =%RSD

Time (Hours)	V4 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1980	1.62E-02	-1.79E+00			13	1.38E-04	0.00E+00
48	1950	1.60E-02	-1.80E+00	5.13E-06	1.38E-04	65	6.91E-04	0.00E+00
168	1944	1.59E-02	-1.80E+00	1.77E-06	4.77E-05	135	1.44E-03	0.00E+00
236	1916	1.57E-02	-1.80E+00	2.22E-06	6.05E-05	136	1.45E-03	0.00E+00
304	1940	1.59E-02	-1.80E+00	1.08E-06	2.92E-05	161	1.71E-03	0.00E+00
348	1882	1.54E-02	-1.81E+00	2.32E-06	6.37E-05	168	1.79E-03	0.00E+00

1935 = Average
33 = St.Dev.
2 =%RSD

Time (Hours)	V5 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	72	5.9E-4	-3.2E+0			0	0.00E+00	0.00E+00
48	5	4.1E-5	-4.4E+0	5.8E-06	2.4E-02	41	4.37E-04	1.13E-04
168	0	0.0E+0	#NUM!	3.9E-06	#NUM!	41	4.33E-04	1.57E-04
236	0	0.0E+0	#NUM!	2.8E-06	#NUM!	44	4.68E-04	1.22E-04
304	0	0.0E+0	#NUM!	2.2E-06	#NUM!	44	4.70E-04	1.20E-04
348	0	0.0E+0	#NUM!	1.9E-06	#NUM!	40	4.21E-04	0.00016893

13 = Average
29 = St.Dev.
226 =%RSD

Time (Hours)	V6 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	110	0.0009031	-3.044284			0	0.00E+00	0.00E+00
48	35	0.0002848	-3.545406	1.288E-05	0.01044	32	3.40E-04	2.79E-04
168	10.	8.201E-05	-4.086111	4.887E-06	0.0062013	46	4.86E-04	3.35E-04
236	0	0	#NUM!	3.827E-06	#NUM!	51	5.46E-04	3.57E-04
304	0	0	#NUM!	2.971E-06	#NUM!	57	6.06E-04	2.97E-04
348	0	0	#NUM!	2.595E-06	#NUM!	54	5.78E-04	3.25E-04

26 = Average
43 = St.Dev.
168 =%RSD

Time (Hours)	V7 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1545	1.3E-2	-1.9E+0			0	0.00E+00	0.00E+00
48	1500	1.2E-2	-1.9E+0	7.63E-06	2.66E-04	80	8.51E-04	0.00E+00
168	1538	1.3E-2	-1.9E+0	3.31E-07	1.14E-05	113	1.20E-03	0.00E+00
236	1460	1.2E-2	-1.9E+0	2.94E-06	1.04E-04	115	1.22E-03	0.00E+00
304	1475	1.2E-2	-1.9E+0	1.87E-06	6.55E-05	170	1.81E-03	0.00E+00
348	1344	1.1E-2	-2.0E+0	4.72E-06	1.73E-04	171	1.82E-03	0.00E+00

1477 = Average
73 = St.Dev.
5 =%RSD

Time (Hours)	V8 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	2082	1.71E-02	-1.77E+00			16	1.70E-04	0.00E+00
48	575	4.72E-03	-2.33E+00	2.57E-04	1.16E-02	153	1.63E-03	1.07E-02
168	554	4.54E-03	-2.34E+00	7.46E-05	3.42E-03	222	2.36E-03	1.02E-02
236	519	4.26E-03	-2.37E+00	5.43E-05	2.56E-03	247	2.63E-03	1.02E-02
304	474	3.89E-03	-2.41E+00	4.34E-05	2.11E-03	291	3.10E-03	1.01E-02
348	438	3.59E-03	-2.44E+00	3.87E-05	1.95E-03	310	3.29E-03	1.02E-02

774 = Average
643 = St.Dev.
83 =%RSD

Time (Hours)	V9 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	424	3.5E-3	-2.5E+0			0	0.00E+00	0.00E+00
48	365	3.0E-3	-2.5E+0	1.00E-05	1.35E-03	48	5.15E-04	0.00E+00
168	328	2.7E-3	-2.6E+0	4.68E-06	6.63E-04	82	8.71E-04	0.00E+00
236	280	2.3E-3	-2.6E+0	5.00E-06	7.63E-04	105	1.11E-03	6.72E-05
304	272	2.2E-3	-2.7E+0	4.09E-06	6.33E-04	128	1.36E-03	0.00E+00
348	229	1.9E-3	-2.7E+0	4.59E-06	7.69E-04	143	1.53E-03	7.31E-05

316 = Average
71 = St.Dev.
22 =%RSD

Time (Hours)	V10 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	432	3.54E-03	-2.45E+00			0	0.00E+00	0.00E+00
48	370	3.03E-03	-2.52E+00	1.05E-05	1.39E-03	42	4.51E-04	5.33E-05
168	347	2.84E-03	-2.55E+00	4.15E-06	5.66E-04	77	8.19E-04	0.00E+00
236	305	2.50E-03	-2.60E+00	4.40E-06	6.39E-04	101	1.08E-03	0.00E+00
304	286	2.34E-03	-2.63E+00	3.93E-06	5.89E-04	112	1.19E-03	3.52E-06
348	263	2.16E-03	-2.67E+00	3.97E-06	6.18E-04	134	1.42E-03	0.00E+00

334 = Average
62 = St.Dev.
19 =%RSD

Time (Hours)	V11 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	1742	1.4E-2	-1.8E+0			0	0.00E+00	0.00E+00
48	1735	1.4E-2	-1.8E+0	1.19E-06	3.63E-05	11	1.17E-04	-5.98E-05
168	1802	1.5E-2	-1.8E+0	-2.94E-06	-8.79E-05	30	3.19E-04	0.00E+00
236	1804	1.5E-2	-1.8E+0	-2.16E-06	-6.44E-05	38	4.04E-04	0.00E+00
304	1795	1.5E-2	-1.8E+0	-1.42E-06	-4.26E-05	43	4.57E-04	0.00E+00
348	1770	1.5E-2	-1.8E+0	-6.67E-07	-2.01E-05	51	5.43E-04	0.00E+00

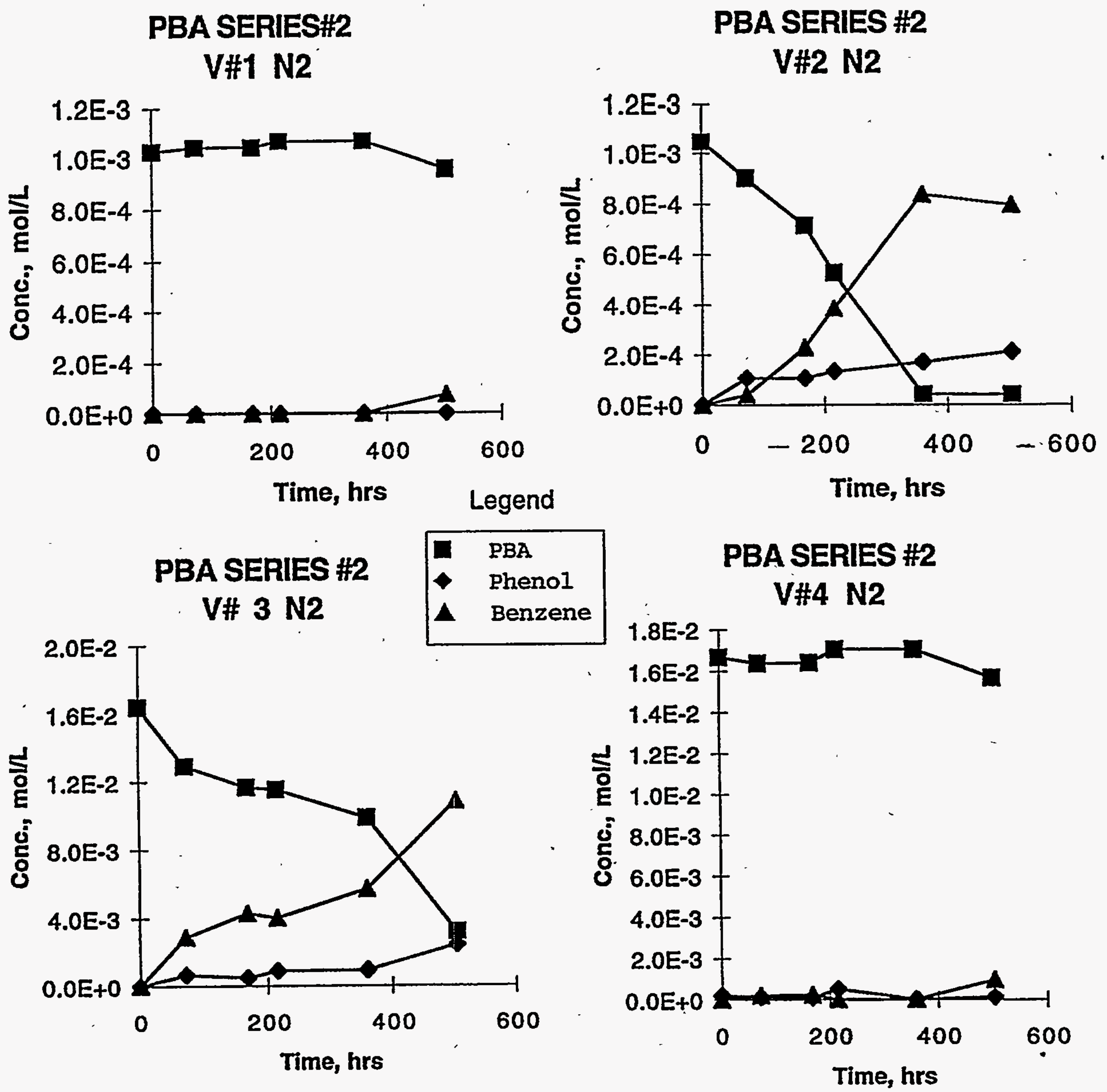
1775 = Average
31 = St.Dev.
2 =%RSD

Time (Hours)	V12 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	423	3.47E-03	-2.46E+00			0	0.00E+00	0.00E+00
48	420	3.44E-03	-2.46E+00	4.37E-07	5.50E-05	0	0.00E+00	2.10E-05
168	430	3.53E-03	-2.45E+00	-3.63E-07	-4.51E-05	0	0.00E+00	0.00E+00
236	426	3.49E-03	-2.46E+00	-1.20E-07	-1.49E-05	0	0.00E+00	0.00E+00
304	444	3.64E-03	-2.44E+00	-5.78E-07	-7.07E-05	0	0.00E+00	0.00E+00
348	440	3.61E-03	-2.44E+00	-4.11E-07	-5.05E-05	0	0.00E+00	0.00E+00

430 = Average
10 = St.Dev.
2 =%RSD

Appendix G
Sample Data From Additional Series #2 PBA Tests

Vessel#	Temp (°C)	Organic (mg/L)	OH- (mole/L)	Total Copper (mg/L)	Other PBA Series#2 Conditions	Initial Rate (mole/L/hr) PBA
Ser.#2, V#1-N2	40	100	0.5	0.1	N2-purge	< 1.0E-06
Ser.#2, V#2-N2	40	100	2.5	10	N2-purge	2.00E-06
Ser.#2, V#3-N2	40	2000	0.5	10	N2-purge	4.80E-05
Ser.#2, V#4-N2	40	2000	2.5	0.1	N2-purge	4.20E-06



Sample Data for Series #2 PBA Tests

Time (Hours)	V1-N2 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	125	1.03E-03	-2.99E+00			0	0.00E+00	0.00E+00
72	127	1.04E-03	-2.98E+00	-2.3E-07	-9.6E-05	0	0.00E+00	0.00E+00
168	127	1.04E-03	-2.98E+00	-9.8E-08	-4.1E-05	0	0.00E+00	0.00E+00
216	130	1.07E-03	-2.97E+00	-1.9E-07	-7.9E-05	0	0.00E+00	0.00E+00
360	130	1.07E-03	-2.97E+00	-1.1E-07	-4.7E-05	0	0.00E+00	0.00E+00
504	116	9.54E-04	-3.02E+00	1.4E-07	6.2E-05	0	0.00E+00	7.11E-05
	126	= Average						
	5	=St. Dev.						
	4	=%RSD						

Time (Hours)	V2-N2 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	128	1.05E-03	-2.98E+00			0	0.00E+00	0.00E+00
72	110	9.02E-04	-3.04E+00	2.03E-06	9.0E-04	10	1.06E-04	3.94E-05
168	87	7.14E-04	-3.15E+00	1.99E-06	9.9E-04	10	1.06E-04	2.28E-04
216	65	5.29E-04	-3.28E+00	2.40E-06	1.4E-03	13	1.33E-04	3.86E-04
360	5	4.10E-05	-4.39E+00	2.91E-06	3.9E-03	16	1.71E-04	8.77E-04
504	5	4.10E-05	-4.39E+00	2.08E-06	2.8E-03	20	2.13E-04	8.35E-04
	67	= Average						
	52	=St. Dev.						
	78	=%RSD						

Time (Hours)	V3-N2 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	2000	1.64E-02	-1.79E+00			0	0.00E+00	0.00E+00
72	1505	1.29E-02	-1.89E+00	4.85E-05	1.4E-03	61	6.53E-04	2.84E-03
168	1423	1.17E-02	-1.93E+00	2.82E-05	8.8E-04	45	4.78E-04	4.25E-03
216	1405	1.15E-02	-1.94E+00	2.26E-05	7.1E-04	82	8.71E-04	4.01E-03
360	1200	9.84E-03	-2.01E+00	1.82E-05	6.2E-04	84	8.94E-04	5.67E-03
504	387	3.17E-03	-2.50E+00	2.62E-05	1.4E-03	225	2.40E-03	1.08E-02
	1320	= Average						
	529	=St. Dev.						
	40	=%RSD						

Time (Hours)	V4-N2 PBA (mg/L)	PBA (mole/L)	log(PBA)	d(PBA)/dt ((mole/L)/hr)	1st order k hr(-1)	Phenol (mg/L)	Phenol (mole/L)	Calculated Benzene (mole/L)
0	2033	1.67E-02	-1.78E+00			17	1.83E-04	0.00E+00
72	1950	1.64E-02	-1.79E+00	4.25E-06	1.1E-04	12	1.23E-04	1.83E-04
168	1996	1.64E-02	-1.79E+00	1.80E-06	4.7E-05	8	8.76E-05	2.15E-04
216	2075	1.70E-02	-1.77E+00	-1.58E-06	-4.1E-05	48	5.11E-04	0.00E+00
360	2076	1.70E-02	-1.77E+00	-9.74E-07	-2.5E-05	5	0.00E+00	0.00E+00
504	1905	1.56E-02	-1.81E+00	2.09E-06	5.6E-05	10	1.06E-04	9.48E-04
	2006	= Average						
	69	=St. Dev.						
	3	=%RSD						

Appendix H - Rate Expression Development Data

3PB Data	
A	2.00E+10
EA	82.2
Cu Order	0.4

v#	1	2	3	4	5	6	7	8	9	10	11	12
temp,C	40	40	40	40	70	70	70	70	55	55	25	25
3PB,ppm	200	200	1800	1800	200	200	1800	1800	600	600	1800	600
OH-, M	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5	1.5	1.5	1.5	1.5
Cu, ppm	0.1	10	10	0.1	10	0.1	0.1	10	1	1	0	0

Time	Measured 3PB concentration as a function of time in mg/L											
0	231	204	1916	2023	210	210	1841	1950	721	722	1990	749
42	231	204	1777	1977	59	200	1726	1264	705	719	1963	749
137.25	230	197	1388	1896	21	181	906	358	633	699	1867	727
305.5	207	161	918	1711	5	115	28.4	5	464	609	1765	673
498.25	201	148	538	1598	5	88	7	5	304	598	1819	680

	Measured ratio of concentration to initial concentration Ca/Cao											
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
42	1.00	1.00	0.93	0.98	0.28	0.95	0.94	0.65	0.98	1.00	0.99	1.00
137.25	1.00	0.97	0.72	0.94	0.10	0.86	0.49	0.18	0.88	0.97	0.94	0.97
305.5	0.90	0.79	0.48	0.85	0.02	0.55	0.02	0.00	0.64	0.84	0.89	0.90
498.25	0.87	0.73	0.28	0.79	0.02	0.42	0.00	0.00	0.42	0.83	0.91	0.91

	Predicted ratio of concentration to initial concentration Cam/Cao											
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
42	0.99	0.96	0.96	0.99	0.50	0.90	0.90	0.50	0.93	0.93	1.00	1.00
137.25	0.98	0.87	0.87	0.98	0.11	0.70	0.70	0.11	0.79	0.79	1.00	1.00
305.5	0.95	0.73	0.73	0.95	0.01	0.45	0.45	0.01	0.59	0.59	1.00	1.00
498.25	0.92	0.60	0.60	0.92	0.00	0.28	0.28	0.00	0.42	0.42	1.00	1.00

2PB Data	
A	3.73E+11
EA	82.1
Cu Order	0.50

v#	1	2	3	4	5	6	7	8	9	10	11	12
temp,C	40	40	40	40	70	70	70	70	55	55	25	25
2pb,ppm	150	150	1600	1600	150	150	1600	1600	500	500	2000	500
OH-, M	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5	1.5	1.5	1.5	1.5
Cu, ppm	0.1	10	10	0.1	10	0.1	0.1	10	1	1	0	0

Measured 2PB concentration as a function of time in mg/L

Time												
0	139	152	1553	1598	156	154	1562	1560	554	569	1612	559
42.5	133	47	432	1103	5	5	139	56	266	219	1441	549
135.5	112	5	37	705	5	5	5	5	127	85	1238	544
183.5	117	5	5	488	5	5	5	5	98	71	1145	510
303.5	115	5	5	316	5	5	5	5	78	47	973	530
375.5	112	5	5	219	5	5	5	5	50	35	910	555

Measured ratio of concentration to intial concentration Ca/Cao

0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
42.5	0.96	0.31	0.28	0.69	0.03	0.03	0.09	0.04	0.48	0.38	0.89	0.98
135.5	0.81	0.03	0.02	0.44	0.03	0.03	0.00	0.00	0.23	0.15	0.77	0.97
183.5	0.84	0.03	0.00	0.31	0.03	0.03	0.00	0.00	0.18	0.12	0.71	0.91
303.5	0.83	0.03	0.00	0.20	0.03	0.03	0.00	0.00	0.14	0.08	0.60	0.95
375.5	0.81	0.03	0.00	0.14	0.03	0.03	0.00	0.00	0.09	0.06	0.56	0.99

Predicted ratio of concentration to initial concentration Cam/Cao

0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
42.5	0.91	0.37	0.37	0.91	0.00	0.21	0.21	0.00	0.26	0.26	1.00	1.00
135.5	0.73	0.04	0.04	0.73	0.00	0.01	0.01	0.00	0.01	0.01	1.00	1.00
183.5	0.65	0.01	0.01	0.65	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00
303.5	0.49	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00
375.5	0.41	0.00	0.00	0.41	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00

PBA Data	
A	4.09E+14
EA	107.5
OH Order	0.7
Cu Order	0.9

Experiment Series #1 for PBA Decomposition

v#	1	2	3	4	5	6	7	8	9	10	11	12
temp	40	40	40	40	70	70	70	70	55	55	25	25
pba,ppm	100	100	2000	2000	100	100	2000	2000	500	500	2000	500
OH-, M	0.5	2.5	0.5	2.5	0.5	2.5	0.5	2.5	1.5	1.5	1.5	1.5
Cu, ppm	0.1	10	10	0.1	10	0.1	0.1	10	1	1	0	0

Measured PBA concentration as a function of time in mg/L

Time												
0	91	80	1583	1969	72	110	1545	2082	424	432	1742	423
48	85	49	1286	1950	0	35	1500	568	350	350	1671	409
168	79	0	833	1944	0	27	1538	554	328	347	1802	437
236	77	0	765	1916	0	0	1460	519	280	305	1804	426
304	78	0	663	1940	0	0	1475	474	272	286	1795	483
348	79	0	653	1882	0	0	1344	438	229	263	1770	445

Measured ratio of concentration to intial concentration - Ca/Cao

0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
48	0.93	0.61	0.81	0.99	0.00	0.32	0.97	0.27	0.83	0.81	0.96	0.97
168	0.87	0.00	0.53	0.99	0.00	0.24	1.00	0.27	0.77	0.80	1.03	1.03
236	0.85	0.00	0.48	0.97	0.00	0.00	0.95	0.25	0.66	0.71	1.04	1.01
304	0.86	0.00	0.42	0.99	0.00	0.00	0.96	0.23	0.64	0.66	1.03	1.14
348	0.86	0.00	0.41	0.96	0.00	0.00	0.87	0.21	0.54	0.61	1.02	1.05

Predicted ratio of concentration to initial concentration - Cam/Cao

0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
48	1.00	0.71	0.90	0.99	0.02	0.82	0.94	0.00	0.82	0.82	1.00	1.00
168	0.99	0.30	0.68	0.98	0.00	0.50	0.80	0.00	0.50	0.50	1.00	1.00
236	0.99	0.19	0.58	0.97	0.00	0.38	0.73	0.00	0.38	0.38	1.00	1.00
304	0.99	0.12	0.50	0.97	0.00	0.28	0.66	0.00	0.29	0.29	1.00	1.00
348	0.99	0.09	0.45	0.96	0.00	0.24	0.63	0.00	0.24	0.24	1.00	1.00

Experiment Series #2 for PBA Decomposition

v#	1	2	3	4
temp	40	40	40	40
pba,ppm	100	100	2000	2000
OH-, M	0.5	2.5	0.5	2.5
Cu, ppm	0.1	10	10	0.1

Time	Measured PBA concentration as a function of time in mg/L			
0	120	128	2000	2033
72	127	110	1505	1882
168	127	87	1423	1996
216	144	65	1405	2362
360	142	0	1239	2076
504	116	0	387	1905

	Measured ratio of concentration to intial concentration - Ca/Cao			
0	1.00	1.00	1.00	1.00
72	1.06	0.86	0.75	0.93
168	1.06	0.68	0.71	0.98
216	1.20	0.50	0.70	1.16
360	1.18	0.00	0.62	1.02
504	0.97	0.00	0.19	0.94

	Predicted ratio of concentration to initial concentration - Cam/Cao			
0	1.00	1.00	1.00	1.00
72	1.00	0.60	0.85	0.99
168	0.99	0.30	0.68	0.98
216	0.99	0.22	0.61	0.98
360	0.99	0.08	0.44	0.96
504	0.98	0.03	0.32	0.95

D.B.Amerine, 241-121H
K. Andringa, 773-41A
M.J.Barnes, 773-A
T.E.Britt, 732-B
J.T.Carter, 704-25S
G.L.Cauthen, 241-119H
W.C.Clark, 704-56H
P.F.Cloessner, 773-A
D.E.Doughty, 704-56H
S.J.Eberlein,704-56H
R.E.Eibling, 704-T
H.H.Elder, 704-S
J.R.Fowler, 241-121H
J.C.Griffin, 773-A
T. Hang, 676-1T
M.J.Hitchler, 992W-1
D.T.Hobbs, 773-A
E.W.Holtzscheiter,773-A
C.W.Hsu, 773-A
M.L.Hyder, 773-A
R.A.Jacobs, 704-T
M.D.Johnson, 704-56H
M.T.Keefer, 704-56H
L.F.Landon, 704-T
T.J.Lex, 719-4A
B.L.Lewis, 703-H
J.C.Marek, 704-T
J.E.Marra, 704-56H
D.J.McCabe, 773-43A
J.D.Menna, 730-2B
M.S.Miller, 704-56H
M.J.Montini, 704-S
J.P.Morin, 719-4A
C.A.Nash, 676-1T
J.K.Norkus, 730-2B
L.M.Papouchado, 773-A
R.A.Peterson, 773-A
M.R.Poirier, 676-T
C.T.Randall, 704-T
R.J.Ray, 773-A
P.L.Rutland, 241-152H
R.M.Satterfield, 719-4A
R.F.Swingle, 773-A
W.L.Tamosaitis, 773-A
G.A.Taylor, 703-H
J.K.Thomas, 730-2B
W.B.VanPelt, 676-1T
D.D.Walker, 773-A
W.R.Wilmarth, 773-42A
A.W.Wiggins, 241-152H
A.L.Wooten, 732-B
G.T.Wright, 773-A
TIM, 703-43A
LWP Files c/o A. Patterson 773-A
ITP Files c/o L. Sumner, 704-56H